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(54) Title: NONIONIC SURFACTANTS AND CARRIERS FROM FATTY GLYCIDYL ETHERS (57) Abstract <p>Nonionic surfactants suitable for use in cleaning compositions and carriers suitable for use in non-aqueous and low-aqueous cleaning compositions are prepared from glycidyl ethers. The acid and base catalyzed processes disclosed herein allow for a wide selection of various alkyl and aryl as well as polyalkylene moieties for inclusion into the nonionic surfactants.</p>		

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NONIONIC SURFACTANTS AND CARRIERS FROM FATTY GLYCIDYL ETHERS

FIELD OF THE INVENTION

The present invention relates to nonionic surfactants and carriers synthesized from monoalkyl ethers of polyethylene glycol and fatty glycidyl ethers, monoalkyl ethers of polyethylene glycol and olefin epoxides or glycidyl ethers derived from monoalkyl ethers of polyethylene glycol with fatty alcohols or ethoxylated fatty alcohols. The present invention further relates to laundry detergent and hard surface cleaning compositions comprising the non-ionic surfactants of the present invention.

BACKGROUND OF THE INVENTION

The use of surfactants for cleaning has been known since ancient times and continues to be an area of intense research interest. The word surfactant is a contraction of the term surface-active agent that was coined in 1950 and has become universally accepted to describe organic substances with certain characteristic features in structure and properties. Surfactants are divided into several categories based on their molecular structure, namely anionic, cationic, nonionic, zwitterionic and ampholytic. Until the modern era of synthetic organic chemistry, known surfactants were comprised almost entirely of the anionic variety.

Based largely on the expanding complexity of modern cleaning compositions, different classes of surfactants have been developed to provide effective dirt and soil removal whether in laundry, personal care or hard surface cleaning applications. Modern surfactants no longer simply act to remove unwanted soil or stains but the surfactant must be compatible with the material or surface to be cleaned. This compatibility translates directly to the concept of not doing damage to the material or surface being cleaned.

Nonionic surfactants, unlike anionic and cationic surfactants, carry no discreet charge when dissolved in aqueous media. They are compatible with ionic and amphoteric surfactants and are generally used in combination with one or more other surfactants. Nonionic surfactants have found wide utility in laundry detergents, household and industrial cleaning products, medical formulations and a wide variety of applications where they are used alone or as an adjunct to ionic surfactants. Their usage is unique in that they can be formulated into non-aqueous or low polarity solutions.

Although linear alkyl alcohols can serve as nonionic surfactants in an extremely limited sense, most modern nonionic surfactants are comprised of ethoxylated aliphatic alcohols, the degree of ethoxylation determining much of the

surface activity and solubility characteristics of the particular target molecule. One problem facing chemists and formulators alike, is the ability to control the number of oxyethylene units, or degree of ethoxylation, in the final product. Normally the degree of ethoxylation is an average value and represents a range of ethoxylation.

A routine method for synthesizing nonionic surfactants that comprises ethoxylated linear alcohols involves treating the parent alcohol with ethylene oxide in the presence of a base catalyst. Those skilled in the art have sought for many years to develop a method that produces nonionic surfactants with a narrow range of ethoxylation values.

Nonionic surfactants derived from ethoxylated linear alcohols typically contain a terminal hydroxyl group which is a key functionality in terms of their inherent physical properties. However, nonionic surfactants comprising an internal secondary alcohol functionality are rare and the present methods for their preparation are tedious and severely limited in scope.

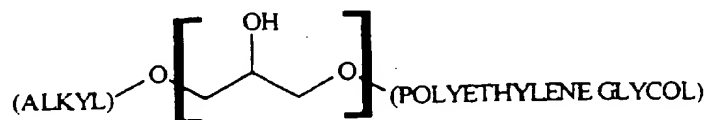
The present invention comprises a method for synthesizing nonionic surfactants comprising an interior secondary alcohol functionality in the form of a 2-hydroxypropoxy moiety while further comprising an ethoxylated segment, said ethoxylated segment may optionally have a wide or narrow statistical distribution of ethyleneoxy residues. The present invention allows for the usage of polyethylene glycols that are of sufficient volatility that they may be pre-purified prior to use and therefore yield a nonionic surfactant having a degree of ethoxylation narrower than the range achievable by ethylene oxide elongation of fatty alcohols. In addition, the hydroxyl group functionality of the propoxy spacer can be further functionalized by the formulator. The nonionic surfactants of the present invention may additionally comprise a terminal hydroxyl moiety.

Adjusting the relative ratio of starting materials leads to nonionic surfactants that comprise two or more polyethylene glycol chains. These materials are themselves non-linear nonionic surfactants and it has been surprisingly found that their incorporation into the surfactant mixture yields a final product with unique and desirable properties.

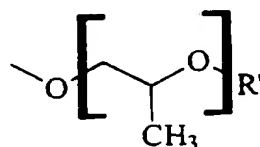
The high degree of synthetic options afforded by the process of the present invention, allows for substitution of the linear alkyl alcohol moiety with other desirable functional chains such as branched alkyl alcohols (guerbet alcohols), cyclic aliphatic (e.g., cyclohexyl alcohols), and di-alkyl substituted aromatic alcohols.

The present invention relates to a novel class of nonionic surfactants comprising the 2-hydroxypropoxy moiety, the 2,5-substituted dioxane moiety and a process for preparing said nonionic surfactants. The 2-hydroxypropyleneoxy moiety

of the present invention has, as one embodiment, the general structure depicted below, which is used for the sole purpose of depicting the said 2-hydroxypropyleneoxy moiety.



The above structure contrasts the 2-hydroxy propyleneoxy functional group of the compounds of the present invention with the propyleneoxy moiety which is derived from propylene oxide and further depicted in the example surfactant below.



This 1,2-propyleneoxy [oxy(methyl-1,2-ethandiyl)] moiety does not comprise the free hydroxyl moiety of the 2-hydroxypropyleneoxy functional group.

In addition, the process of the present invention can be modified by the formulator to produce nonionic surfactants that are 2,5-disubstituted dioxanes.

It is also a purpose of the present invention to provide solid, liquid, semi-solid (i.e., gel form) hard surface cleaning compositions comprising the nonionic surfactants of the present invention.

It is a further purpose of the present invention to provide granular and liquid laundry detergent compositions comprising the nonionic surfactants of the present invention.

It is still a further purpose of the present invention to provide nonionic surfactants that are suitable for use in medical compositions as a carrier, surfactant, suspending agent, or adjunct ingredient.

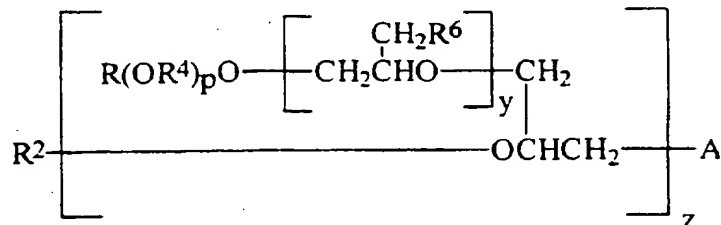
BACKGROUND ART

Published Patent documents describing the preparation and use of nonionic surfactants in laundry and hard surface cleaning compositions include: U.S. Patent No. 4,248,729, issued February 3, 1981; U.S. Patent No. 4,284,532, issued August 18, 1981; U.S. Patent No. 4,627,927, issued December 9, 1986; U.S. Patent No. 4,790,856, issued December 13, 1988; U.S. Patent No. 4,804,492, issued February 14, 1989; U.S. Patent No. 4,770,815, issued September 13, 1989; U.S. Patent No. 5,035,814, issued July 30, 1991; U.S. Patent No. 5,047,165, issued September 10, 1991; Patent No. 5,419,853, issued May 30, 1995; GB Application No. 2,144,763, published March 13, 1985; GB Application No. 2,154,599, published September 9,

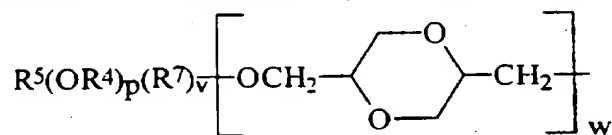
1985; WO Application No. 9,296,150, published April 16, 1992; EP Application No. 342,177, published November 15, 1989.

SUMMARY OF THE INVENTION

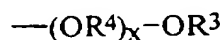
The present invention relates to nonionic surfactants of the formula:



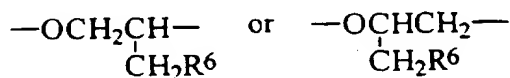
wherein R is C₁-C₂₂ linear alkyl, C₃-C₂₂ branched alkyl, C₃-C₂₂ linear alkenyl, C₃-C₂₂ branched alkenyl, C₅-C₂₂ cyclic alkyl, C₅-C₂₂ cyclic alkenyl, aryl or C₁-C₂₂ alkyl substituted aromatic; R² is hydrogen, C₁-C₄ alkyl, or when z = 0, the formula:



wherein R⁴ is C₂-C₄ alkylene; R⁵ is hydrogen or R; A has the formula:



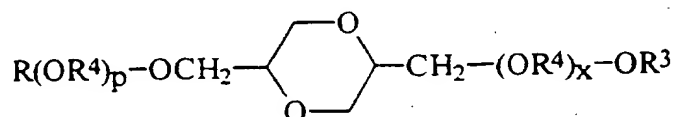
wherein R³ is hydrogen or R; R⁷ has the formula:



wherein R⁶ is A, halogen, or hydroxyl; p is from 0 to 100; v is 0 or 1; w is 0 or 1; x is from 0 to 100; y is from 0 to 2; z is from 0 to 3; w + z is at least 1.

The present invention also relates to processes for preparing the above described nonionic surfactants of the present invention.

The present invention further relates to nonionic surfactants of the formula:



wherein R is C₁-C₂₂ linear alkyl, C₃-C₂₂ branched alkyl, C₃-C₂₂ linear alkenyl, C₃-C₂₂ branched alkenyl, C₅-C₂₂ cyclic alkyl, C₅-C₂₂ cyclic alkenyl, aryl or C₁-C₂₂ alkyl substituted aromatic; R³ is hydrogen, C₁-C₂₂ alkyl or alkenyl; R⁴ is C₂-C₄ alkylene; p is from 0 to 100; x is from 0 to 100.

The present invention further relates to novel nonionic solvents useful for carriers, as non-aqueous cleaning solvents, or as surfactant boosters.

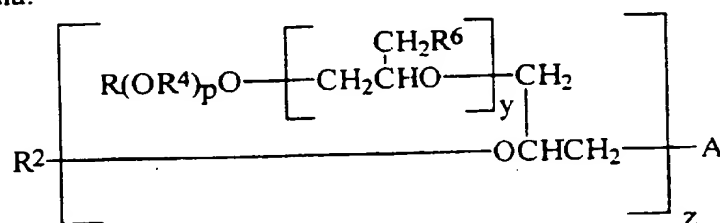
The present invention further relates to cleaning compositions comprising at least 0.01% of the nonionic surfactants described herein.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius ($^{\circ}\text{C}$) unless otherwise noted. All documents cited are incorporated herein by reference.

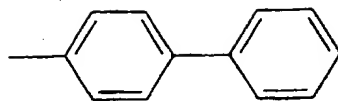
DETAILED DESCRIPTION OF THE INVENTION

1. Nonionic Surfactant Compounds:

The present invention comprises compounds that are the reaction products of glycidyl ethers and polyethylene glycols of olefin epoxides and polyethylene glycols in the presence of an acid or a base catalyst. The present invention also comprises compounds that result from the reaction of alcohols, polyethylene glycols and epihalohydrins in the presence of either a base or in the presence of an acid and a base catalyst in separate steps. The nonionic surfactants of the present invention have the formula:



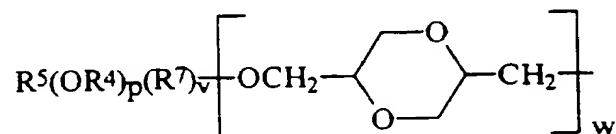
wherein R units are linear alkylene moieties comprising from 1 to about 22 carbon atoms, branched alkylene moieties comprising from 3 to about 22 carbon atoms, linear alkenylene moieties comprising from 3 to about 22 carbon atoms, branched alkenylene moieties comprising from 3 to about 22 carbon atoms, cyclic alkylene moieties comprising from 5 to about 22 carbon atoms with at least 3 carbon atoms comprising the alkylene ring. R units are also comprised of one or more aromatic rings. The aromatic rings can be fused or bonded in series or can be linked by an alkyl chain or the aromatic rings may be alkyl substituted as in the case of 1,4-phenylene moieties provide that the total number of carbon atoms in the rings and pendant chains does not exceed 22 carbon atoms in number. An example of a fused aromatic ring is naphthalene. This adduct can be suitably attached to an alkyl chain or can be bonded directly to the oxygen atom of the ROH alcohol. Bonding of the aromatic and substituted aromatic rings can be at any ring position. R can also be one or more aromatic rings connected in series, for example, two benzene rings bonded to one another by a covalent bond, for example, a bi-phenyl moiety of the formula:



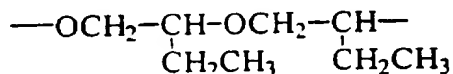
R is also any aromatic ring, whether fused or joined in series by covalent bonding that is substituted by one or more alkyl groups provided the total number of carbon atoms in the R moiety does not exceed 22.

R units comprise C_1 - C_{22} linear alkyl, C_3 - C_{22} branched alkyl, C_3 - C_{22} linear alkenyl, C_3 - C_{22} branched alkenyl, C_5 - C_{22} cyclic alkyl, C_5 - C_{22} cyclic alkenyl, aryl or C_1 - C_{22} alkyl substituted aromatic moieties. Preferred R units are linear alkyl, branched alkyl and alkyl substituted aromatic. Preferred linear alkyl moieties comprise C_6 - C_{20} "fatty" alkyl, more preferably the C_6 - C_{18} "fatty" alkyl chains. Preferred branched alkyl groups are the 2-alkyl substituted C_8 - C_{22} "Guerbet" alkyl chains. Examples of Guerbet alkyl chains are 2-ethylhexyl, 2-propylheptyl, 2-butyloctyl and 2-pentylnonyl. Preferred alkyl substituted aromatic groups comprise 4-alkylphenyl, and 1,4-dialkyl substituted phenyl compounds (1,4-phenylene). Examples include 4-octylphenyl, 4-nonylphenyl, 4-methylbenzyl, 4-ethylphenyl and 2-(4-methylphenyl)ethyl. More preferred is 4-nonylphenyl.

R^2 units are hydrogen, alkyl groups comprising 1-4 carbon atoms (such as methyl, ethyl, propyl, butyl) or moieties of the formula

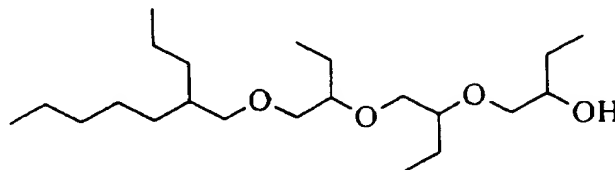


wherein R^4 is a C_2 - C_4 alkylene moiety such that the $-(OR^4)-$ unit comprises, for example, ethyleneoxy, propyleneoxy, butyleneoxy, 2-methylethyleneoxy units and mixtures thereof. Preferred R^4 is ethylene. For example, if an R^4 units comprises 2 moles of a C_2 - C_4 alkylene oxides such as butylene oxide, this results in the R^4 unit having the general formula:

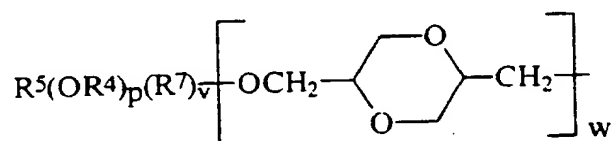


The addition of a C_2 - C_4 alkylene oxide moiety can be accomplished after the nonionic surfactant backbone is assembled as an optional replacement for the R^2 hydrogen atom. The C_2 - C_4 alkylene oxide moieties may also be introduced into the molecule as a pre-formed adduct combined with the R moiety in the form of an

$R(OR^4)_pOH$ alcohol reactant. An example of an $R(OR^4)_pOH$ alcohol of this type where R^4 is derived from 1,2-butyleneoxide, R is a C_{10} "Guerbet" alkyl moiety, and the index p is equal to 3, has the formula:

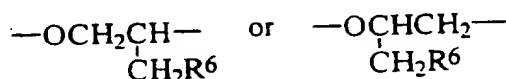


The nonionic surfactants of the present invention have the value of p from 0 to about 100, preferably from about 4 to about 24, more preferably from about 4 to about 12. Preferably R^2 is hydrogen and when R^2 has the formula



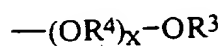
preferably the R^5 unit is equal to R and the indices p and v are both equal to 0 and w is equal to 0 or 1. For the cases where R^5 is C_1 - C_4 alkyl, p is preferably 2 to 100, more preferably 4 to 50, most preferably 4 to 12. For nonionic surfactants of the present invention that are derivatives of 2,5-disubstituted dioxanes, described further herein below, preferably the indices p and v are equal to 0 and w is equal to 1.

R^7 units have the formula:



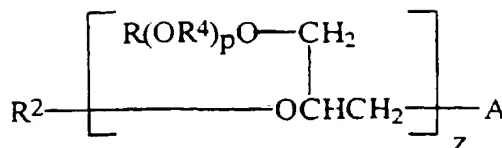
wherein R^6 is R , halogen, or hydroxyl. R^6 is preferably halogen, most preferably chlorine.

For the nonionic surfactants of the present invention A units are polyethylene glycols units having the formula:



wherein R^3 is hydrogen, C_1 - C_4 alkylene or alkenylene, preferably R^3 units are methyl. The R^4 units comprising A are the same as those described herein above. The value of x is from 0 to 100, preferably from 2 to 20, most preferably from 4 to 12.

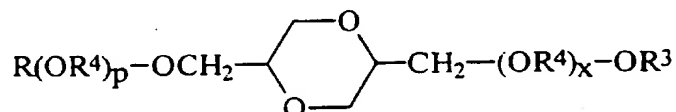
For nonionic surfactants of the present invention having the general formula



there is a need for at least one of the R, R² or A moieties to have a hydrophobic character and in addition for at least one of the R, R² or A moieties to have a hydrophilic character in order for the compounds of the present invention to exhibit surfactant behavior. These hydrophilic and hydrophobic portions can be introduced in separate reaction steps, such as the capping of the R² hydroxy moiety, or they can be introduced as a pre-formed adducts as in the case of alkoxyated fatty alcohols, i.e. R(OR⁴)_pOH alcohols, or the glycidyl ether of alkoxyated fatty alcohols.

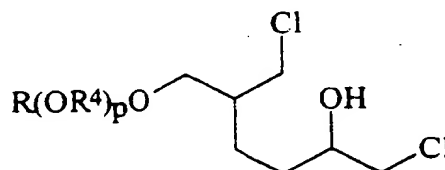
The value of y is from 0 to 2, preferably 0. The value of z is 0, 1, 2 or 3, preferably 1 or 2, more preferably 1.

The present invention also relates to nonionic surfactants of the following formula:

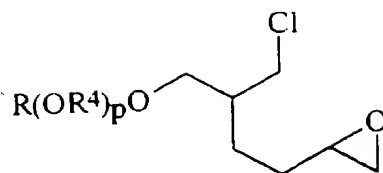


that comprise the 2,5-disubstituted dioxane moiety and which are formed by the process of the present invention. This process, further described herein below, allows the formulator to form the 2,5-disubstituted dioxanes rather than the 2-hydroxypropoxy compounds described herein above.

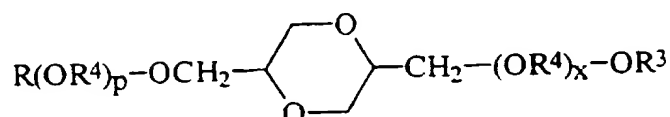
While not wishing to be limited by theory, these 2,5-disubstituted dioxane units are formed when two equivalents of an epihalohydrin are condensed with one equivalent of an R(OR⁴)_pOH or R³O(R⁴O)_xH unit to form an intermediate having the formula



wherein the moiety R³O(R⁴O)_x- can be interchanged or substituted for R(OR⁴)_pO- in the structure above. This intermediate is then treated with a base to re-form a glycidyl ether of the structure

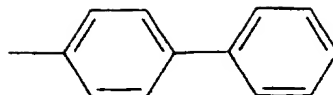


The above intermediate can further react with one equivalent of an $R(OR^4)_pOH$ or $R^3O(R^4O)_xH$ moiety, in the presence of a base, to form a 2,5-disubstituted dioxane having the structure



In the example depicted herein above, one equivalent of $R(OR^4)_pOH$ and $R^3O(R^4O)_xH$ is used, however the formulator may chose two equivalents of the same moiety, for example two moles of $R(OR^4)_pOH$. The above example represents R^5 equal to R and the indices m , v , y , and z all having the value 0; w is equal to 1. For the case of 2,5-di-substituted dioxanes of the present invention, the values of R , R^3 , and R^4 units and the indices p and x are further described herein below.

The 2,5-disubstituted dioxane embodiment comprises R units are linear alkylene moieties comprising from 1 to about 22 carbon atoms, branched alkylene moieties comprising from 3 to about 22 carbon atoms, linear alkenylene moieties comprising from 3 to about 22 carbon atoms, branched alkenylene moieties comprising from 3 to about 22 carbon atoms, cyclic alkylene moieties comprising from 5 to about 22 carbon atoms with at least 3 carbon atoms comprising the alkylene ring. R units are also comprised of one or more aromatic rings. The aromatic rings can be fused or bonded in series or can be linked by an alkyl chain or the aromatic rings may be alkyl substituted as in the case of 1,4-phenylene moieties provide that the total number of carbon atoms in the rings and pendant chains does not exceed 22 carbon atoms in number. An example of a fused aromatic ring is naphthalene, which can be suitably attached to an alkyl chain or can be bonded directly to the oxygen atom. Bonding of the aromatic and substituted aromatic rings can be at any ring position. R is also one or more aromatic rings connected in series, for example, two benzene rings bond to one another by a covalent bond, for example, a bi-phenyl moiety of the formula:



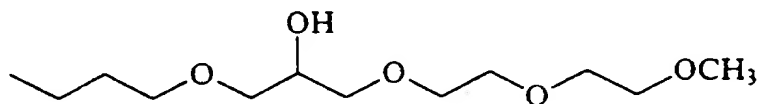
R is also any aromatic ring, whether fused or joined in series by covalent bonding that is substituted by one or more alkyl groups provided the total number of carbon atoms in the R moiety does not exceed 22.

Preferred R units are linear alkyl, branched alkyl and alkyl substituted aromatic. Preferred linear alkyl moieties comprise C_6 - C_{20} "fatty" alkyl, more preferably the C_6 - C_{18} "fatty" alkyl chains. Preferred branched alkyl groups are the 2-alkyl substituted C_8 - C_{22} "guerbet" alkyl chains. Examples of guerbet alkyl chains are 2-ethylhexyl, 2-propylheptyl, 2-butyloctyl and 2-pentylononyl. Preferred alkyl substituted aromatic groups comprise 4-alkylphenyl, and 1,4-dialkyl substituted phenyl compounds. Examples include 4-octylphenyl, 4-nonylphenyl, 4-methylbenzyl, 4-ethylphenyl and 2-(4-methylphenyl)ethyl.

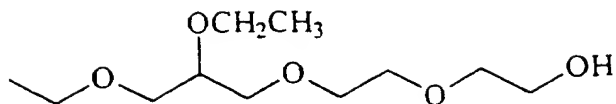
R^3 is hydrogen or R, preferred R^3 is selected from the group consisting essentially of methyl, ethyl, propyl, butyl, and mixtures thereof. R^4 is a C_2 - C_4 alkylene moiety such that the moiety $-(OR^4)-$ comprises, for example ethyleneoxy, propyleneoxy, butyleneoxy units and mixtures thereof; preferred R^4 is ethylene. The value of p is from 0 to about 100, preferably from about 6 to about 24, more preferably from about 6 to about 12.

The compounds of the present invention may also be use as nonionic solvents useful as carriers, as non-aqueous cleaning solvents, or as surfactant boosters. For example, compounds of the present invention having p equal to 0 and x from 1 to about 4, wherein R is C_1 - C_6 linear or branched alkyl; R^2 is hydrogen, methyl, ethyl or mixtures thereof; and R^3 is methyl or ethyl, can be used in as carriers and co-solvents in a number of non-aqueous or low-aqueous cleaning applications.

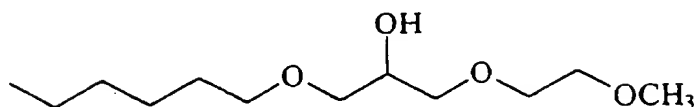
An example of a non-aqueous or low-aqueous cleaning solvent according to the present invention has the formula



Further examples of non-aqueous or low-aqueous cleaning solvents according to the present invention has the formula



and the formula



For the purposes of the present invention the term "non-aqueous cleaning compositions" is defined as cleaning compositions that comprise no water or only small amounts of water (generally less than 1-3%) that is used in processing. For the purposes of the present invention the term "low-aqueous cleaning compositions" is defined as cleaning compositions wherein the amount of water present is less than 50% of the liquid carriers or solvents.

The cleaning compositions of the present invention comprise at least 0.01%, preferably 0.1% to 50%, more preferably 1% to about 10% by weight of detergent surfactant.

The cleaning compositions of the present invention comprise carriers and other adjunct materials. The a partial list of the adjunct materials suitable for use in the practice of the present invention are further listed herein below. The cleaning compositions of the present invention also optionally comprise carriers. Typically liquid carriers comprise water but other suitable carriers are such solvents as methanol, ethanol, n-propanol, isopropanol and the like which are commonly used in hard surface cleaning compositions. Surprisingly, the nonionic surfactants of the present invention can be used in conjunction with low aqueous carrier, that is, carriers that comprise less than 50% water. Additionally, the nonionic surfactants of the present invention can be used with other solvents and in non-aqueous modes of delivery.

A preferred non-classical solvent for use herein is butoxypropoxypropanol (BPP), methoxypropoxypropanol (MPP), ethoxypropoxypropanol (EPP), propoxypropoxypropanol (PPP), butoxypropanol, tributoxypropanol and all isomers and mixtures thereof. Additional solvents include C₄-C₆ polyethylene glycol derivatives, examples of which are hexylene glycol, hexylene diglyme and butylene diglycol. Most preferred is BPP and when used in conjunction with the nonionic surfactants of the present invention in cleaning compositions comprising 1,2-octanediol, the amount of the latter material can be minimized. Moreover, it allows for the formulation of effective cleaning compositions comprising the nonionic

surfactants of the present invention without the use of water or conventional solvents.

Carriers are not limited to liquids and may comprise filler salts and perlite abrasives in the case of hard surface cleaners having general scouring application. Inert ingredients such as silicon dioxide and pumice are also compatible with the nonionic surfactants of the present invention. The use of the nonionic surfactants of the present invention in gels and lanolin based carrier systems is also an acceptable embodiment. Preferred lotion and cream embodiments comprise, for example, white petrolatum, cetyl alcohol, stearyl alcohol, Sorbitan monooleate, Sorbitan monostearate, Macrogol 400, Macrogol 4000 and the like as further described in *Surfactant Systems: Their chemistry, pharmacy and biology*, Attwood, D.; and Florence, A.T.; Chapman and Hall (1983), incorporated herein by reference in its entirety.

Fig. I is an example of a preferred embodiment of the present invention wherein R is a C₁₂ linear alkyl group, R² is hydrogen, R³ is methyl, x is 6, y is 0 and z is 1.

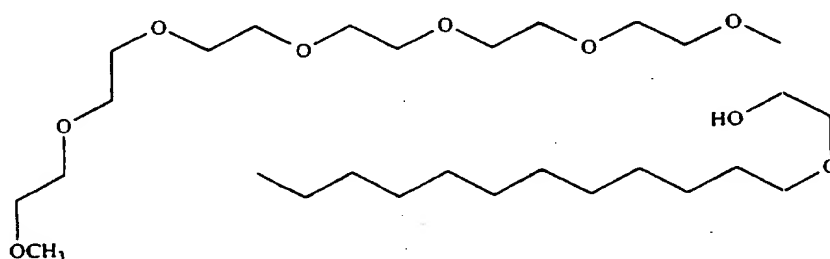


Fig. I

Fig. II represents an embodiment of the present invention wherein R is a C₁₀ guerbet alkyl group, R² is hydrogen, R³ is methyl, x is 4, y is 1 and z is 1.

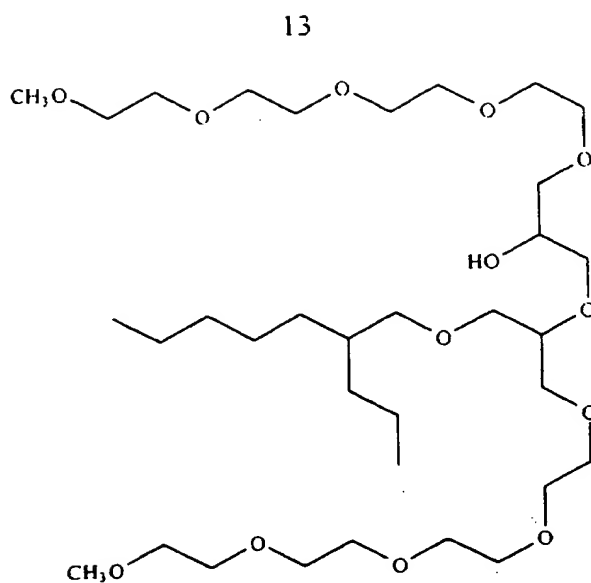


Fig. II

Fig. III represents an embodiment wherein R is an alkyl substituted phenyl group (i.e., (4-nonyl)phenyl) R² is methyl, R³ is methyl, p is 0, x is 3, y is 0 and z is 1.

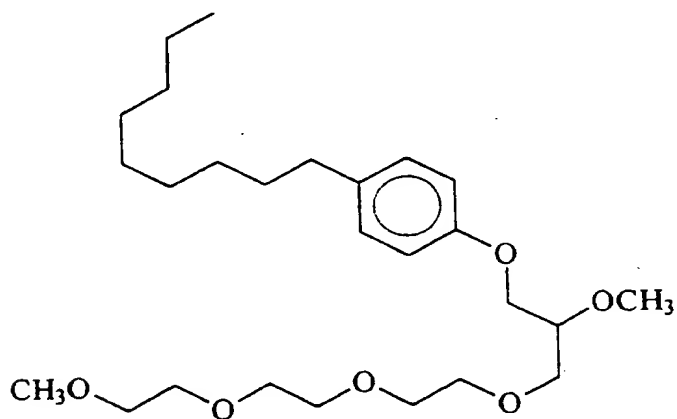


Fig. III

Fig IV represents an embodiment wherein R is linear alkyl (n-hexyl), R² is hydrogen, R³ is methyl, x is 16, y is 0 and z is 2.

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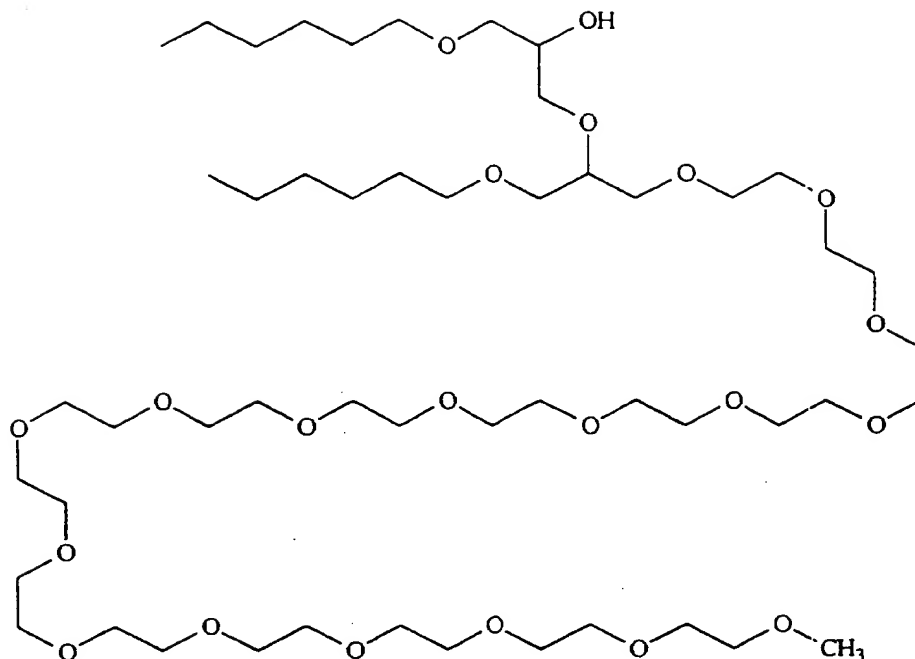


Fig. IV

Fig. V represents an embodiment of the present invention wherein R is hexyl, R³ is methyl, R⁵ is R, p is equal to 0, x is equal to 3, v is equal to 0, w is equal to 1, y is equal to 0, and z is equal to 0.

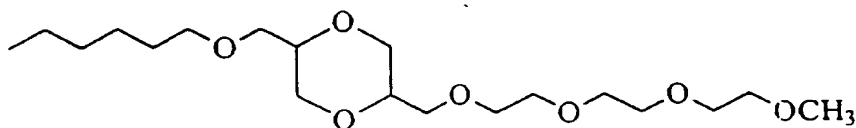


Fig. V

2. Preparation of nonionic surfactants

The present invention comprises the methods for preparing the nonionic surfactants of the present invention. For the processes of the present invention the term "base" means any alkaline reagent suitable for the required de-protonation of a hydroxyl moiety. Examples of suitable bases include, but is not limited to, sodium metal, potassium metal, sodium hydride, potassium hydride, sodium hydroxide, potassium hydroxide and other like inorganic hydroxides. Preferred bases are sodium metal, sodium hydride, more preferred is sodium metal. Where alkoxides

derived from materials of relatively low volatility are desired, KOH and NaOH are preferred bases because water can be removed by heat and/or vacuum.

In the processes of the present invention the term "acid" means any acidic substance or reagent capable of catalyzing the required epoxide ring opening reactions or other like catalysts. Examples of acids suitable for the processes of the present invention are hydrochloric acid, sulfuric acid, methanesulfonic acid and Lewis acids. Preferred are the Lewis acids, most preferred Lewis acids are boron trifluoride, gaseous or as a complex such as boron trifluoride etherate, stannic chloride and titanium tetrachloride. The acids used in the neutralization steps of the processes of the present invention are not required to be the same acids that are used for the purpose of catalyzing the epoxide ring opening reactions. The acids used for the neutralization step form inorganic salts that are acceptable for remaining in the product or are salts that are easily removed during the optional purification steps. A preferred acid used for neutralization is methanesulfonic acid.

In the process examples recited herein, epichlorohydrin is used as an example of an epihalohydrin. However, epibromohydrin or epiodohydrin are both suitable for the processes of the present invention. Preferred halohydrin is epichlorohydrin.

The processes disclosed in the present invention, while yielding the 2-hydroxypropyleneoxy moiety, also offer methods by which the formulator may functionalize the hydroxyl group, R², typically by capping with an alkyl group or by alkoxylation.

The processes disclosed in the present invention further provide the formulator with optional purification steps. Depending upon the application or use of the nonionic surfactant, the formulator may seek purity of a varying degree. For example, a nonionic surfactant prepared for use as a medical adjunct may require a narrower range of ethoxylation or higher level of purity not necessary or desirable for other applications. In addition, embodiments of the present invention that are intended for application in low aqueous or non-aqueous systems, and hence have a low tolerance for residual inorganic materials, can be optionally neutralized by acids or bases that are suitable for removal by non-aqueous techniques. The nonionic surfactants of the present invention can be prepared by several processes described herein. In general, the product of the reaction will afford nonionic surfactants of suitable purity such that the surfactants may be used without further purification. It has also been surprisingly found that minor reaction by-products when left in the product matrix, enhance the desired properties of certain nonionic surfactants when used in specific surfactant applications. As an example, the formation of branched,

bis-polyethylene glycol surfactants such as those depicted in figures II and III, constitutes a desirable product mixture of certain nonionic surfactants that result in increased cleaning performance in certain cleaning applications.

a) Synthesis of Nonionic Surfactants from Pre-formed Glycidyl Ethers.

Preparation of "Simple" 2-hydroxypropoxy surfactants. The nonionic surfactants of the present invention can be prepared using pre-formed glycidyl ethers. These pre-formed glycidyl ethers are available from various commercial sources (i.e. Aldrich Chemical Co.) or they can be easily prepared, isolated and purified by methods known to those skilled in the art. Polyethylene glycol monomethyl ethers (i.e., MPEG 350 and MPEG 550) are also available from commercial sources (Aldrich Chemical Co.) in high purity and known degree of ethoxylation. The reaction of glycidyl ethers and polyethylene glycols for the preparation of the nonionic surfactants of the present invention, is depicted in Scheme I:

Scheme I

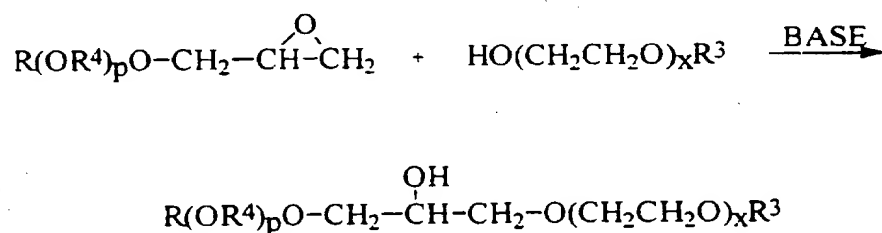
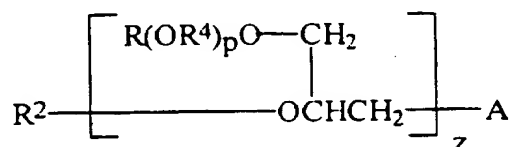


fig. VI

A process for preparing the nonionic surfactants of the present invention depicted in the example shown in Scheme I having the formula:

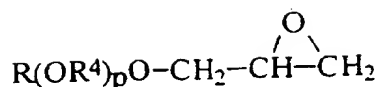


wherein A has the formula:



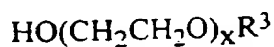
wherein x is from 0 to about 100; p is from 0 to 100; z is equal to 1; R² is hydrogen or C₁-C₄ alkyl; R³ is C₁-C₄ alkyl or C₁-C₄ alkenyl; R⁴ is C₂-C₄ alkyl; comprising the steps of:

- a) reacting a glycidyl ether of the formula



linear
C₂₂

wherein R is C₁-C₂₂ linear alkyl, C₃-C₂₂ branched alkyl, C₃-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, C₅-C₂₂ cyclic alkyl, aryl or C₁-alkyl substituted aryl; with an alkyl capped polyethylene glycol of the formula:



wherein R³, p and x are as defined above; in the presence of a base to form a crude alkaline nonionic surfactant reaction product;

- b) optionally neutralizing the crude alkaline nonionic surfactant reaction product formed in step (a) to form a crude nonionic surfactant reaction product;
- c) optionally further reacting the reaction product of step (a) or (b) wherein R² is hydrogen with
 - i) an alkylating agent whereby R² is converted to a C₁-C₄ alkyl moiety; said alkyl moiety selected from the group consisting of methyl, ethyl, propyl, butyl, and mixtures thereof; or
 - ii) a C₁-C₄ alkylene oxide whereby R² is converted to an C₁-C₄ hydroxyalkyl moiety or polyoxyalkylene moiety;
- d) optionally purifying the reaction product formed in step (b); or
- e) optionally purifying the reaction product formed in step (c).

A further example of the process of the present invention, provides for the optional replacement of the hydrogen atom of the secondary hydroxyl group with an alkyl moiety as depicted in Scheme II.

Scheme II

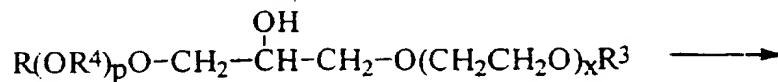
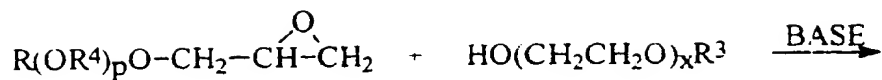


fig. VI

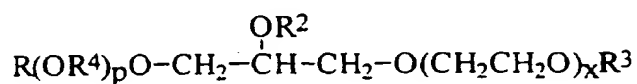
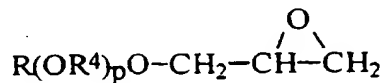


fig. VII

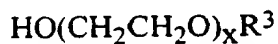
In a preferred embodiment of the process depicted in Scheme II, the resulting 2-hydroxypropyloxy nonionic surfactant is further reacted to convert the R² hydrogen moiety to an alkyl moiety, said process comprises the steps of:

- a) reacting a glycidyl ether of the formula



linear
C₂₂

wherein R is C₁-C₂₂ linear alkyl, C₃-C₂₂ branched alkyl, C₃-C₂₂ alkenyl, C₄-C₂₂ branched alkenyl, C₅-C₂₂ cyclic alkyl, aryl or C₁-alkyl substituted aryl; p = 0 - 20 with an alkyl capped polyethylene glycol of the formula:



wherein x is from 2 to 20, R³ is methyl; in the presence of a base to form a crude alkaline nonionic surfactant reaction product;

- b) optionally:

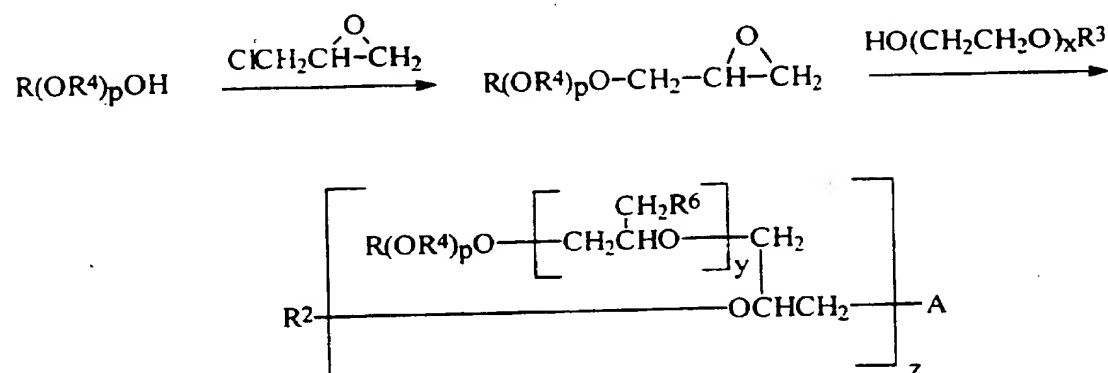
- i) neutralizing the crude alkaline nonionic surfactant reaction product formed in step (a) to form a crude nonionic surfactant reaction product; or
- ii) adding sufficient base to convert the R² functionality to an alkoxide; and

- c) optionally further reacting the reaction product of step (b) (ii) wherein R^2 is converted to a C_1 - C_4 alkyl moiety by reaction with a C_1 - C_4 alkyl halide.

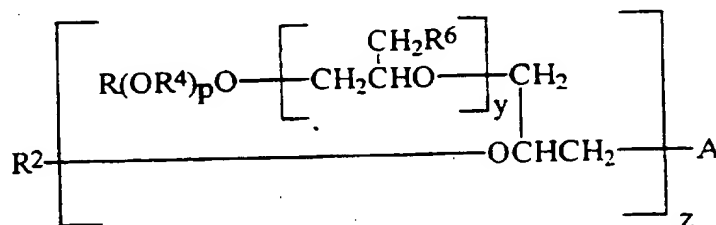
The alkylating agents suitable for converting the R^2 substituent from a hydrogen atom, as depicted in Fig. VI above, to a C_1 - C_4 alkyl moiety are those typically used by one skilled in the art. For example, methyl chloride, dimethyl sulfate, ethyl bromide, propyl iodide and butyl methanesulfonate are suitable for use in converting the R^2 group from a hydrogen atom to a C_1 - C_4 alkyl group such as methyl, ethyl, propyl and butyl respectively.

b) Synthesis from Glycidyl Ethers formed *in situ*.

Scheme III

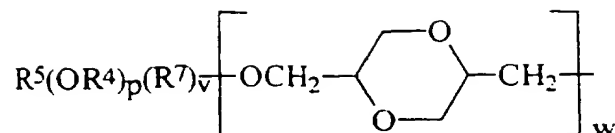


A process of the present invention for preparing a nonionic surfactant as depicted in Scheme III, of the formula:

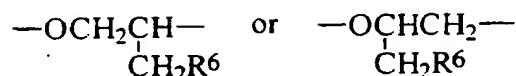


wherein R^2 has the formula

20



R^7 has the formula:

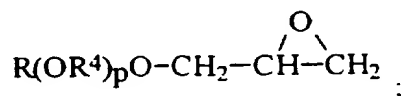


wherein R^6 is R or halogen; A has the formula:

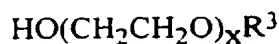


wherein R^3 is C_1 - C_4 alkyl or C_3 - C_4 alkenyl; x is from 0 to 100; p is from 0 to 100; v is 0 or 1; w is 0 or 1; x is from 2 to about 100; y is 0, 1 or 2; z is from 0 to 3; w + z is greater than 1; comprising the steps of:

- a) reacting an alcohol of the formula $R(OR^4)_pOH$ wherein R is C_1 - C_{22} linear alkyl, C_4 - C_{22} branched alkyl, C_5 - C_{22} cyclic alkyl, C_5 - C_{22} cyclic alkenyl, aromatic, or C_1 - C_{22} alkyl substituted aromatic; with an epihalohydrin first in the presence of an acid catalyst, then in the presence of sufficient base to form a glycidyl ether of the formula



- b) neutralizing the reaction;
c) reacting the glycidyl ether formed in step (a) with a C_1 - C_4 alkyl capped polyethylene glycol ether of the formula:



wherein R^3 and x is the same as defined above, using an acid catalyst to form an acidic crude nonionic surfactant reaction product;

- d) neutralizing acidic reaction product formed in step (b) to form a crude nonionic surfactant product;
e) optionally further reacting the reaction product of step (c) wherein R^2 is hydrogen with sufficient base to convert the R^2 moiety to an alkoxide intermediate, followed by treatment with either:
i) an alkylating agent whereby R^2 is converted to a C_1 - C_4 alkyl moiety; said alkyl moiety selected from the group consisting of methyl, ethyl, propyl, butyl, and mixtures thereof; or

- ii) a C₂-C₄ alkylene oxide whereby R² is converted to an C₂-C₄ hydroxyalkyl moiety or polyoxyalkylene moiety;
- f) optionally purifying the reaction product formed in step (c); or
- g) optionally purifying the reaction product formed in step (d).
- c) Synthesis of 2,5-disubstituted dioxane Nonionic Surfactants. Other nonionic surfactants that are suitably prepared by the process of the present invention are those comprising the 2,5-disubstituted dioxane ring system wherein treatment of the alcohol ROH with an excess of epihalohydrin and a Lewis acid catalyst is followed in a second chemical process step by treatment of the reaction solution with polyethylene glycol in the presence of a base catalyst. Scheme IV depicts the formation of these 2,5-disubstituted dioxane polyethylene glycol nonionic surfactants as represented by figure VIII.

Scheme IV

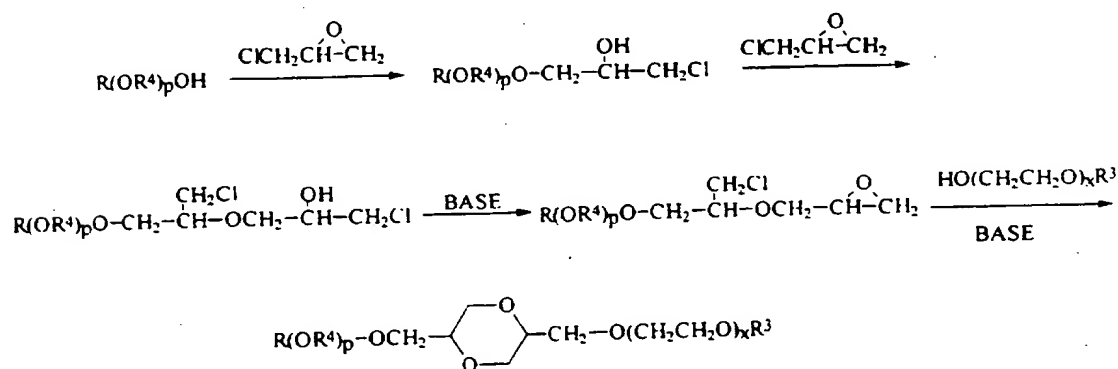
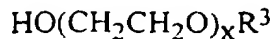


fig. VIII

The process for preparing non linear nonionic surfactants of the present invention as depicted in Scheme IV comprises the steps of:

- a) reacting an alcohol of the formula ROH wherein R is C₁-C₂₂ linear alkyl, C₄-C₂₂ branched alkyl, C₅-C₂₂ cyclic alkyl, C₅-C₂₂ alkenyl, aromatic, or C₁-C₂₂ alkyl substituted aromatic; with 1 to 5 equivalents of an epihalohydrin in the presence of an acid catalyst and glycidyl treatment with at least one equivalent of base to form a crude ether mixture:

- b) reacting the crude glycidyl ether mixture formed in step (a) with 1 to 3 equivalents of a C₁-C₄ alkyl capped polyethylene glycol ether of the formula:

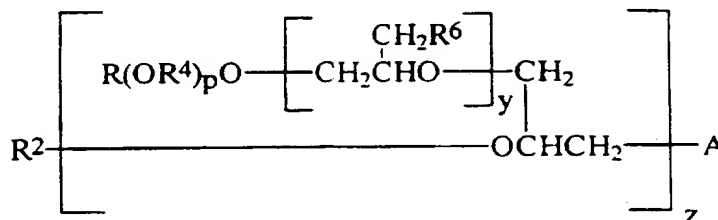


wherein R³ and x is the same as defined above, with sufficient base to form an crude nonionic surfactant reaction mixture;

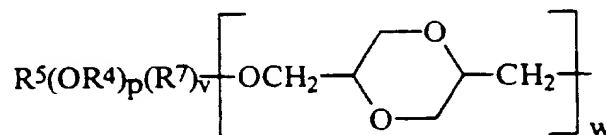
- c) neutralizing alkaline reaction mixture formed in step (b) to form a crude nonionic surfactant product; and
d) optionally isolating the reaction product formed in step (c).

d) Synthesis of Nonionic Surfactants from Epihalohydrin, Alcohols and Polyethylene Glycolmonoether. Nonionic surfactants of the present invention can be prepared using epihalohydrin, an alcohol ROH, and the monoalkyl ether of polyethylene glycol.

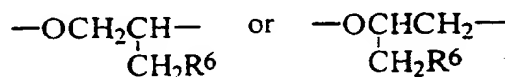
A process of the present invention for preparing a nonionic surfactant of the formula:



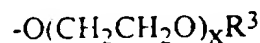
wherein R² has the formula



R⁷ has the formula:

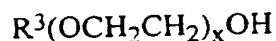


wherein R⁶ is hydroxyl or halogen; A has the formula:

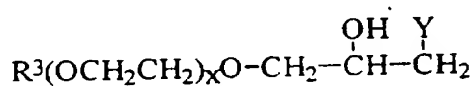


wherein R^3 is C_1 - C_4 alkyl or C_3 - C_4 alkenyl; x is from 0 to 100; p is from 0 to 100; v is 0 or 1; w is 0 or 1; x is from 2 to about 100; y is 0, 1 or 2; z is 1, 2 or 3; $w + z$ is at least 1; comprising the steps of:

- a) reacting an alcohol of the formula:

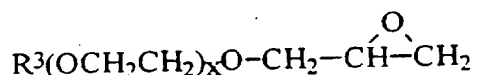


wherein R^3 and x are as defined above; and an epihalohydrin in the presence of acid catalyst to form an acidic crude halohydrin reaction product of the formula

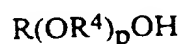


wherein Y is chlorine, bromine, or iodine;

- b) optionally purifying the crude halohydrin reaction product formed in step (a);
c) reacting the halohydrin reaction product of step (a) or step (b) with at least one equivalent of base to form a glycidyl ether of the formula



- d) reacting the glycidyl ether formed in step (c) with a capped polyethylene glycol of the formula



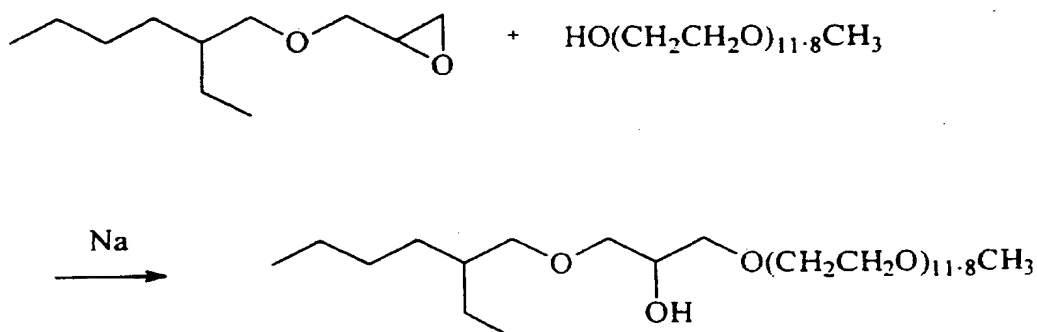
linear wherein R is C_1 - C_{22} linear alkyl, C_3 - C_{22} branched alkyl, C_3 - C_{22} alkenyl, C_3 - C_{22} branched alkenyl, C_5 - C_{22} cyclic alkyl, C_5 - C_{22} cyclic alkenyl, aryl or C_1 - C_{22} alkyl substituted aromatic; in the presence of sufficient base to form an alkaline crude nonionic surfactant reaction product;

- e) neutralizing the alkaline reaction product formed in step (d) to form a crude nonionic surfactant reaction product;
f) optionally further reacting the reaction product of step (e) wherein R^2 is hydrogen with sufficient base to convert the R^2 moiety to an alkoxide then further reacting the crude product from step (e) with either:

- i) an alkylating agent whereby R^2 is converted to a C_1 - C_4 alkyl moiety; said alkyl moiety selected from the group consisting of methyl, ethyl, propyl, butyl, and mixtures thereof; or
- ii) a C_1 - C_4 alkylene oxide whereby R^2 is converted to an C_1 - C_4 hydroxyalkyl moiety or polyoxyalkylene moiety;
- g) optionally purifying the reaction product formed in step (e); or
- h) optionally purifying the reaction product formed in step (f).

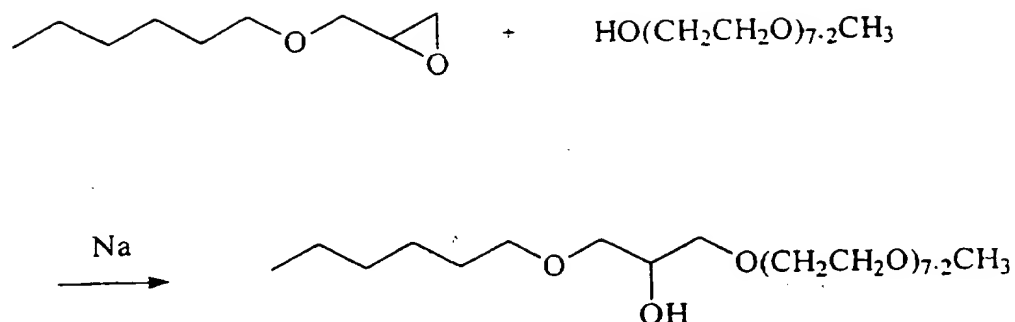
The following are examples of the preparation of the nonionic surfactants of the present invention.

Example I



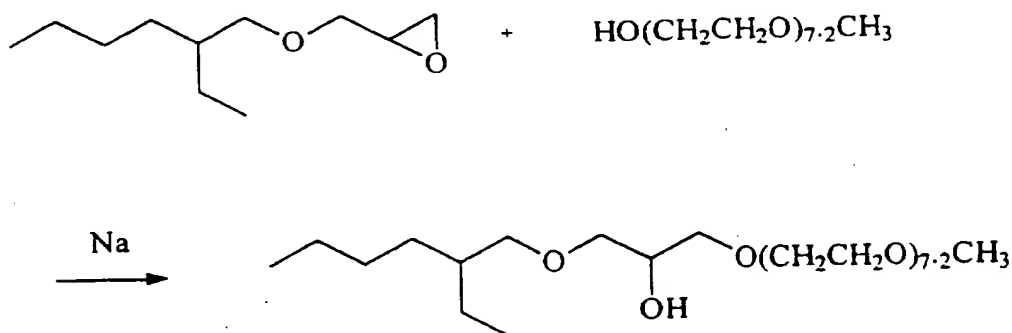
Polyethylene glycol monomethyl ether comprising 11.8 ethoxylate units per mole (MPEG-550) (73.9 gm, 0.134 mol) and sodium metal (0.31 gm, 0.014 gm-atm) is weighed into a 250 mL 3-neck round bottom flask equipped with a magnetic stirring bar, modified Claisen head, reflux condenser and thermometer, and is heated to 120° C under argon blanketing, for two hours or until the sodium is completely consumed. 2-ethyl-hexylglycidyl ether (25.0 gm, 0.134 mol) is added and the solution is stirred at 120° C for six hours. At this point the solution pH is approximately 11. The solution is then neutralized with methanesulfonic acid and centrifuged to remove the salts. Yield is approximately 83 gm.

Example II



Polyethylene glycol monomethyl ether comprising 7.2 ethoxylate units per mole (MPEG-350) (55.1 gm, 0.126 mol) and sodium metal (0.29 gm, .013 gm-atm) is weighed into a 250 mL 3-neck round bottom flask equipped with a magnetic stirring bar, modified Claisen head, reflux condenser and thermometer, and is heated to 120° C under argon blanketing, for two hours or until the sodium is completely consumed. Hexyl-glycidyl ether (20.0 gm, 0.126 mol) is added and the solution is stirred at 120° C for six hours. At this point the solution pH is approximately 12. The solution is then neutralized with methanesulfonic acid and centrifuged to remove the salts. Yield is approximately 61 gm.

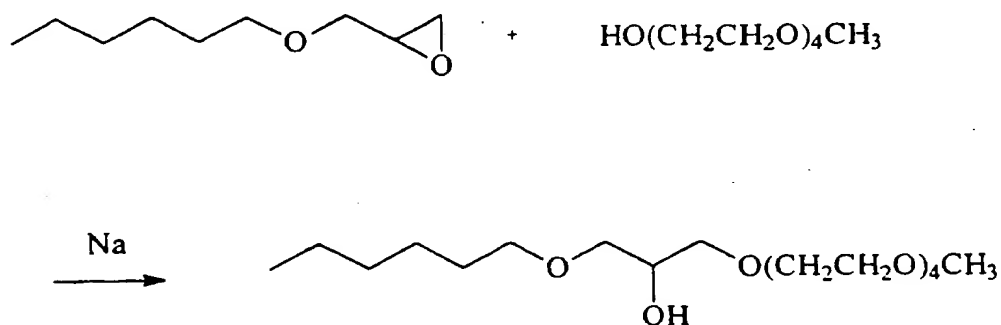
Example III



Polyethylene glycol monomethyl ether comprising 7.2 ethoxylate units per mole (MPEG-350) (47.0 gm, 0.134 mol) and sodium metal (0.31 gm, 0.013 gm-atm) is weighed into a 250 mL 3-neck round bottom flask equipped with a magnetic stirring bar, modified Claisen head, reflux condenser and thermometer, and is heated to 120° C under argon blanketing, for two hours or until the sodium is completely

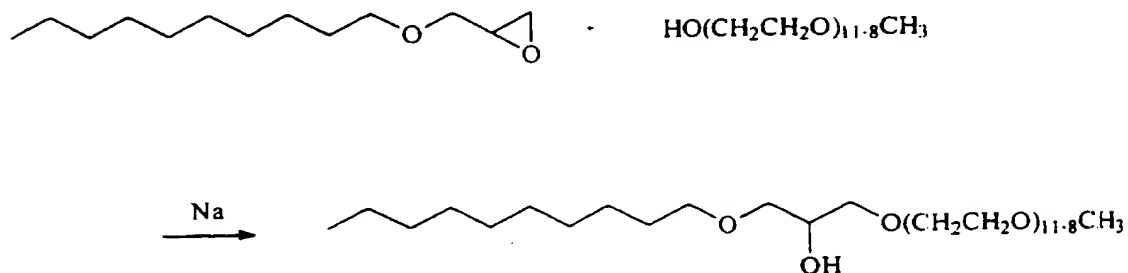
consumed. 2-ethyl-hexylglycidyl ether (25.0 gm, 0.134 mol) is added and the solution is stirred at 120° C for six hours. At this point the solution pH is approximately 12. The solution is then neutralized with methanesulfonic acid and centrifuged to remove the salts. Yield is approximately 63 gm.

Example IV



Polyethylene glycol monomethyl ether comprising 4 ethoxylate units per mole (MPEG-208) (25.0 gm, 0.120 mol) and sodium metal (0.4 gm, 0.017 gm-atm) is weighed into a 250 mL 3-neck round bottom flask equipped with a magnetic stirring bar, modified Claisen head, reflux condenser and thermometer, and is heated to 120° C under argon blanketing, for two hours or until the sodium is completely consumed. Hexyl-glycidyl ether (19.0 gm, 0.120 mol) is added and the solution is stirred at 120° C for six hours. At this point the solution pH is approximately 12. The solution is then neutralized with methanesulfonic acid and centrifuged to remove the salts. Yield is approximately 34 gm.

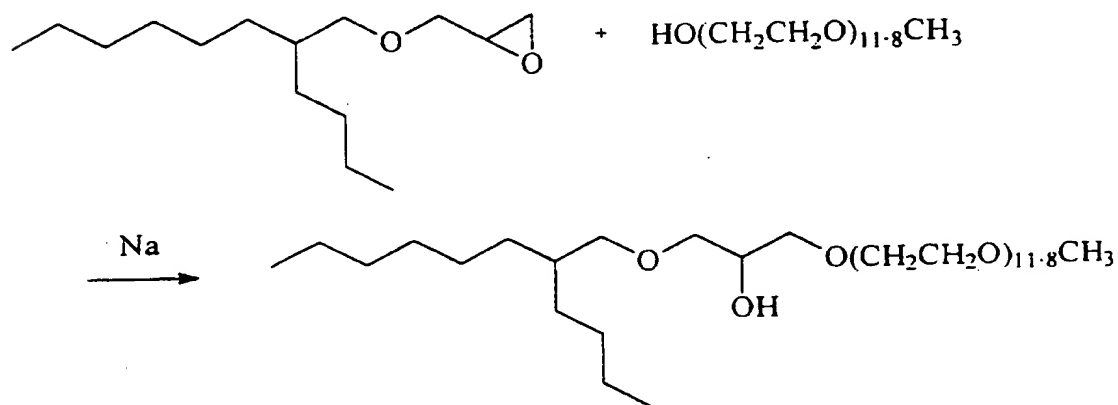
Example V



Polyethylene glycol monomethyl ether comprising 11.8 ethoxylate units per mole (MPEG-550) (70.0 gm, 0.127 mol) and sodium metal (0.29 gm, 0.0126 gm-

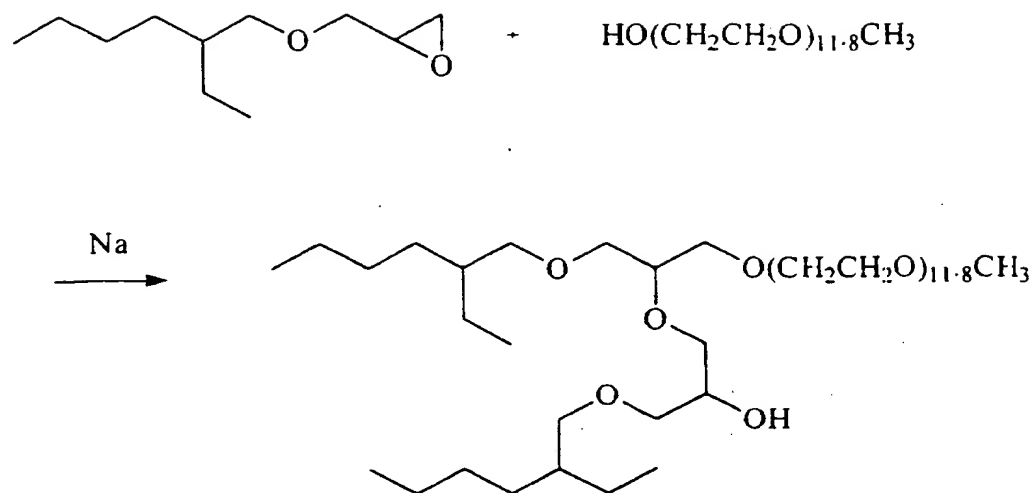
atm) is weighed into a 250 mL 3-neck round bottom flask equipped with a magnetic stirring bar, modified Claisen head, reflux condenser and thermometer, and is heated to 120° C under argon blanketing, for two hours or until the sodium is completely consumed. Decyl-glycidyl ether (27.0 gm, 0.126 mol) is added and the solution is stirred at 120° C for six hours. At this point the solution pH is approximately 12. The solution is then neutralized with methanesulfonic acid and centrifuged to remove the salts. Yield is approximately 67 gm.

Example VI



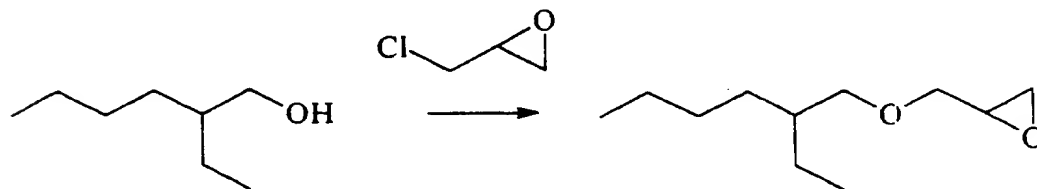
Polyethylene glycol monomethyl ether comprising 11.8 ethoxylate units per mole (MPEG-550) (70.0 gm, 0.127 mol) and sodium metal (0.29 gm, 0.0126 gm-atm) is weighed into a 250 mL 3-neck round bottom flask equipped with a magnetic stirring bar, modified Claisen head, reflux condenser and thermometer, and is heated to 120° C under argon blanketing, for two hours or until the sodium is completely consumed. 2-butyldecyl-glycidyl ether (30.5 gm, 0.126 mol) is added and the solution is stirred at 120° C for six hours. At this point the solution pH is approximately 12. The solution is then neutralized with methanesulfonic acid and centrifuged to remove the salts. Yield is approximately 73 gm.

Example VII



Polyethylene glycol monomethyl ether comprising 11.8 ethoxylate units per mole (MPEG-550) (70.0 gm, 0.127 mol) and sodium metal (0.29 gm, 0.0126 gm-atm) is weighed into a 250 mL 3-neck round bottom flask equipped with a magnetic stirring bar, modified Claisen head, reflux condenser and thermometer, and is heated to 120° C under argon blanketing, for two hours or until the sodium is completely consumed. 2-ethyl-hexylglycidyl ether (47.4 gm, 0.268 mol) is added and the solution is stirred at 120° C for six hours. At this point the solution pH is approximately 11. The solution is then neutralized with methanesulfonic acid and centrifuged to remove the salts. Yield is approximately 83 gm.

EXAMPLE VIII



To a 5 L 3-neck flask equipped with a reflux condenser, overhead mechanical stirrer, thermometer, a heating mantle, a means for controlling the reaction temperature (I²R Thermowatch®) and dropping funnel is charged 2-ethyl-1-hexanol (2000 gm., 15.4 mole) and approximately 10 gm. of stannic chloride. Epichlorohydrin (1132 gm., 12.3 mole) was then added dropwise via the addition

funnel at such a rate that the temperature does not exceed 70° C. The reaction is allowed to cool to room temperature under an atmosphere of nitrogen. After stirring overnight, 3 gms additional stannic chloride is added and the solution is heated to 65° C for 7 hours. The reaction is allowed to cool to room temperature under an atmosphere of nitrogen. After stirring overnight the reaction is heated the next day an additional 7 hours at 65° C. The completeness of the reaction is determined by ¹H NMR. NaOH (520 gm., 13 mole) is dissolved in 1500 mL water and the resulting solution is added slowly to the reaction mixture with good stirring. The reaction is heated to 90° C for 1.5 hours. The reaction is then cooled to room temperature and the aqueous layer removed. The organic phase is extracted three times with water. The residual water is removed from the organic layer by heating to 95° C with nitrogen sparging. The crude epoxide is then purified by fractional distillation under reduced pressure. After separation of the residual fatty alcohol from the crude epoxide mixture, in excess of 1700 gm 3-[(2-ethyl)hexoxy]-1,2-epoxypropane is achieved.

The laundry detergents and hard surface cleaning compositions of the present invention may comprise one or more of the following ingredients.

Detergative Surfactants - Nonlimiting examples of surfactants, including other nonionic surfactants, useful herein typically at levels from about 1% to about 50%, by weight, include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃⁻M⁺)CH₃ and CH₃(CH₂)_y(CHOSO₃⁻M⁺)CH₂CH₃ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C₁₀-18 glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like, can also be included in the overall compositions. The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl)

glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

ADJUNCT INGREDIENTS

Enzymes - Enzymes can be included in the present detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from surfaces such as textiles or dishes, for the prevention of refugee dye transfer, for example in laundering, and for fabric restoration. Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

"Detergent enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry, hard surface cleaning or personal care detergent composition. Preferred detergent enzymes are hydrolases such as proteases, amylases and lipases. Preferred enzymes for laundry purposes include, but are not limited to, proteases, cellulases, lipases and peroxidases. Highly preferred for automatic dishwashing are amylases and/or proteases, including both current commercially available types and improved types which, though more and more bleach compatible through successive improvements, have a remaining degree of bleach deactivation susceptibility.

Enzymes are normally incorporated into detergent or detergent additive compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics, dishware and the like. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Higher active levels may also be desirable in highly concentrated detergent formulations.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE® and SAVINASE® from Novo and MAXATASE® from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Novo.

In more detail, an especially preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in the patent applications of A. Baeck, et al. entitled "Protease-Containing Cleaning Compositions" having US Serial No. 08/322,676, and C. Ghosh, et al. "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, both filed October 13, 1994.

Amylases suitable herein, especially for, but not limited to automatic dishwashing purposes, include, for example, α -amylases described in GB 1,296,839 to Novo; RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo. FUNGAMYL® from Novo is especially useful. Engineering of enzymes for improved stability, e.g., oxidative stability, is known. See, for example J. Biological

Chem., Vol. 260, No. 11, June 1985, pp 6518-6521. These preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide / tetraacetythylenediamine in buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as about 60°C; or alkaline stability, e.g., at a pH from about 8 to about 11, measured versus the above-identified reference-point amylase. Stability can be measured using any of the art-disclosed technical tests. See, for example, references disclosed in WO 9402597. Stability-enhanced amylases can be obtained from Novo or from Genencor International. One class of highly preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the *Bacillus* amylases, especially the *Bacillus* α -amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors. Oxidative stability-enhanced amylases vs. the above-identified reference amylase are preferred for use, especially in bleaching, more preferably oxygen bleaching, as distinct from chlorine bleaching, detergent compositions herein. Such preferred amylases include (a) an amylase according to the hereinbefore incorporated WO 9402597, Novo, Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine, preferably threonine, of the methionine residue located in position 197 of the *B.licheniformis* alpha-amylase, known as TERMAMYL®, or the homologous position variation of a similar parent amylase, such as *B. amyloliquefaciens*, *B.subtilis*, or *B.stearothermophilus*; (b) stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8, 15, 197, 256, 304, 366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Other particularly preferred oxidative stability enhanced amylase include those described in WO 9418314 to Genencor International and WO 9402597 to Novo. Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases. Other preferred enzyme modifications are accessible. See WO 9509909 A to Novo.

Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. 4,435,307, Barbesgoard et al, March 6, 1984, discloses suitable fungal cellulases from *Humicola insolens* or *Humicola*

strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® (Novo) is especially useful. See also WO 9117243 to Novo.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open Feb. 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano." or "Amano-P." Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE® enzyme derived from *Humicola lanuginosa* and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein. Lipase and amylase variants stabilized against peroxidase enzymes are described in WO 9414951 A to Novo. See also WO 9205249 and RD 94359044.

Cutinase enzymes suitable for use herein are described in WO 8809367 A to Genencor.

Peroxidase enzymes may be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen peroxide, etc., for "solution bleaching" or prevention of transfer of dyes or pigments removed from substrates during the wash to other substrates present in the wash solution. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases such as chloro- or bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed in WO 89099813 A, October 19, 1989 to Novo and WO 8909813 A to Novo.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971. Gedge

et al, EP 199,405 and EP 200,586. October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

Enzyme Stabilizing System - Enzyme-containing, including but not limited to, liquid compositions, herein may comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detergent enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition.

One stabilizing approach is the use of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. Calcium ions are generally more effective than magnesium ions and are preferred herein if only one type of cation is being used. Typical detergent compositions, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 8 to about 12 millimoles of calcium ion per liter of finished detergent composition, though variation is possible depending on factors including the multiplicity, type and levels of enzymes incorporated. Preferably water-soluble calcium or magnesium salts are employed, including for example calcium chloride, calcium hydroxide, calcium formate, calcium malate, calcium maleate, calcium hydroxide and calcium acetate; more generally, calcium sulfate or magnesium salts corresponding to the exemplified calcium salts may be used. Further increased levels of Calcium and/or Magnesium may of course be useful, for example for promoting the grease-cutting action of certain types of surfactant.

Another stabilizing approach is by use of borate species. See Severson, U.S. 4,537,706. Borate stabilizers, when used, may be at levels of up to 10% or more of the composition though more typically, levels of up to about 3% by weight of boric acid or other borate compounds such as borax or orthoborate are suitable for liquid detergent use. Substituted boric acids such as phenylboronic acid, butaneboronic acid, p-bromophenylboronic acid or the like can be used in place of boric acid and

reduced levels of total boron in detergent compositions may be possible though the use of such substituted boron derivatives.

Stabilizing systems of certain cleaning compositions may further comprise from 0 to about 10%, preferably from about 0.01% to about 6% by weight, of chlorine bleach scavengers, added to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from about 0.5 ppm to about 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme, for example during dish- or fabric-washing, can be relatively large; accordingly, enzyme stability to chlorine in-use is sometimes problematic. Since perborate or percarbonate, which have the ability to react with chlorine bleach, may present in certain of the instant compositions in amounts accounted for separately from the stabilizing system, the use of additional stabilizers against chlorine, may, most generally, not be essential, though improved results may be obtainable from their use. Suitable chlorine scavenger anions are widely known and readily available, and, if used, can be salts containing ammonium cations with sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Likewise, special enzyme inhibition systems can be incorporated such that different enzymes have maximum compatibility. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired. In general, since the chlorine scavenger function can be performed by ingredients separately listed under better recognized functions, (e.g., hydrogen peroxide sources), there is no absolute requirement to add a separate chlorine scavenger unless a compound performing that function to the desired extent is absent from an enzyme-containing embodiment of the invention; even then, the scavenger is added only for optimum results. Moreover, the formulator will exercise a chemist's normal skill in avoiding the use of any enzyme scavenger or stabilizer which is majorly incompatible, as formulated, with other reactive ingredients, if used. In relation to the use of ammonium salts, such salts can be simply admixed with the detergent composition but are prone to adsorb water and/or liberate ammonia during storage. Accordingly,

such materials, if present, are desirably protected in a particle such as that described in US 4,652,392, Baginski et al.

Bleaching Compounds - Bleaching Agents and Bleach Activators - The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxypropionic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

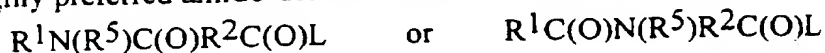
A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with

silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Mixtures of bleaching agents can also be used.

Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

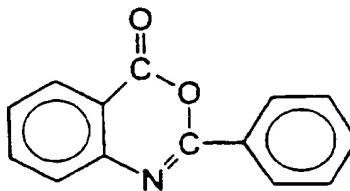
Highly preferred amido-derived bleach activators are those of the formulae:



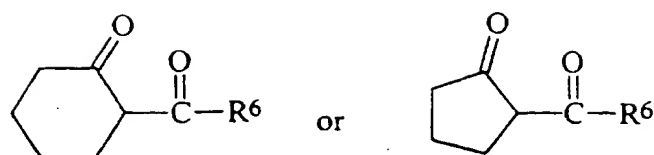
wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R^6 is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include $Mn^{IV}_2(u-O)_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(PF_6)_2$, $Mn^{III}_2(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(ClO_4)_2$, $Mn^{IV}_4(u-O)_6(1,4,7\text{-triazacyclononane})_4(ClO_4)_4$, $Mn^{III}Mn^{IV}_4(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(ClO_4)_3$, $Mn^{IV}(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})-(OCH_3)_3(PF_6)$, and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will

preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

Builders - Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% builder. Liquid formulations typically comprise from about 5% to about 50%, more typically about 5% to about 30%, by weight, of detergent builder. Granular formulations typically comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

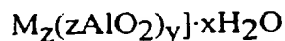
Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric metaphosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- Na_2SiO_5 morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- Na_2SiO_5 (NaSKS-6 form) is most preferred for

use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

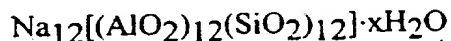
Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S.

Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al. on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Chelating Agents - The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Clay Soil Removal/Anti-redeposition Agents - The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties. Granular detergent compositions which contain these compounds typically contain from about 0.01% to about 10.0% by weight of the water-soluble ethoxylates amines; liquid detergent compositions typically contain about 0.01% to about 5%.

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986. Another group of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985. Other clay soil removal and/or anti redeposition agents known in the art can also be utilized in the compositions herein. Another type of preferred antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Suds Suppressors - Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such

as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about -40°C and about 50°C, and a minimum boiling point not less than about 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below about 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms. The term "paraffin," as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M. S.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al, and in U.S. Patent 4,652,392, Baginski et al, issued March 24, 1987.

An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of:

- (i) polydimethylsiloxane fluid having a viscosity of from about 20 cs. to about 1,500 cs. at 25°C;
- (ii) from about 5 to about 50 parts per 100 parts by weight of (i) of siloxane resin composed of $(\text{CH}_3)_3\text{SiO}_{1/2}$ units of SiO_2 units in a ratio of from $(\text{CH}_3)_3\text{SiO}_{1/2}$ units and to SiO_2 units of from about 0.6:1 to about 1.2:1; and
- (iii) from about 1 to about 20 parts per 100 parts by weight of (i) of a solid silica gel.

In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), or polypropylene glycol. The primary silicone suds suppressor is branched/crosslinked and preferably not linear.

To illustrate this point further, typical liquid laundry detergent compositions with controlled suds will optionally comprise from about 0.001 to about 1, preferably from about 0.01 to about 0.7, most preferably from about 0.05 to about 0.5, weight % of said silicone suds suppressor, which comprises (1) a nonaqueous emulsion of a primary antifoam agent which is a mixture of (a) a polyorganosiloxane, (b) a resinous siloxane or a silicone resin-producing silicone compound, (c) a finely divided filler material, and (d) a catalyst to promote the reaction of mixture components (a), (b) and (c), to form silanolates; (2) at least one nonionic silicone surfactant; and (3) polyethylene glycol or a copolymer of polyethylene-polypropylene glycol having a solubility in water at room temperature of more than about 2 weight %; and without polypropylene glycol. Similar amounts can be used in granular compositions, gels, etc. See also U.S. Patents 4,978,471, Starch, issued December 18, 1990, and 4,983,316, Starch, issued January 8, 1991, 5,288,431, Huber et al., issued February 22, 1994, and U.S. Patents 4,639,489 and 4,749,740, Aizawa et al at column 1, line 46 through column 4, line 35.

The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene glycol/polypropylene glycol, all having an average molecular weight of less than about 1,000, preferably between about 100 and 800. The polyethylene glycol and polyethylene/polypropylene copolymers herein have a solubility in water at room temperature of more than about 2 weight %, preferably more than about 5 weight %.

The preferred solvent herein is polyethylene glycol having an average molecular weight of less than about 1,000, more preferably between about 100 and 800, most preferably between 200 and 400, and a copolymer of polyethylene

glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between about 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol:copolymer of polyethylene-polypropylene glycol.

The preferred silicone suds suppressors used herein do not contain polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block copolymers of ethylene oxide and propylene oxide, like PLURONIC L101.

Other suds suppressors useful herein comprise the branched alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. Secondary alcohols include the C₆-C₁₆ alkyl alcohols having a C₁-C₁₆ chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

For any detergent compositions to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine. Suds suppressors, when utilized, are preferably present in a "suds suppressing amount. By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines.

The compositions herein will generally comprise from 0% to about 5% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to about 5%, by weight, of the detergent composition. Preferably, from about 0.5% to about 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically utilized in amounts up to about 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.25% to about 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from about 0.1% to about 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from about

0.01% to about 5.0%, although higher levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished compositions.

Fabric Softeners - Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 4,062,647, Storm and Nirschl, issued December 13, 1977, as well as other softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 10% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. Patent 4,375,416, Crisp et al. March 1, 1983 and U.S. Patent 4,291,071, Harris et al, issued September 22, 1981.

Polymeric Soil Release Agent - Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions and processes of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

The polymeric soil release agents useful herein especially include those soil release agents having: (a) one or more nonionic hydrophile components consisting essentially of (i) polyoxyethylene segments with a degree of polymerization of at least 2, or (ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophile segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or (iii) a mixture of oxyalkylene units comprising oxyethylene and from 1 to about 30 oxypropylene units wherein said mixture contains a sufficient amount of oxyethylene units such that the hydrophile component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fiber surfaces upon deposit of the soil release agent on such surface, said hydrophile segments preferably comprising at least about 25% oxyethylene units and more preferably, especially for such components having about 20 to 30 oxypropylene units, at least about 50% oxyethylene units; or (b) one or more hydrophobe components comprising (i) C₃ oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate:C₃ oxyalkylene terephthalate units is about 2:1 or lower, (ii) C₄-C₆ alkylene or oxy C₄-C₆ alkylene segments, or mixtures

therein. (iii) poly (vinyl ester) segments, preferably polyvinyl acetate), having a degree of polymerization of at least 2, or (iv) C₁-C₄ alkyl ether or C₄ hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C₁-C₄ alkyl ether or C₄ hydroxyalkyl ether cellulose derivatives, or mixtures therein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C₁-C₄ alkyl ether and/or C₄ hydroxyalkyl ether units to deposit upon conventional polyester synthetic fiber surfaces and retain a sufficient level of hydroxyls, once adhered to such conventional synthetic fiber surface, to increase fiber surface hydrophilicity, or a combination of (a) and (b).

Typically, the polyoxyethylene segments of (a)(i) will have a degree of polymerization of from about 200, although higher levels can be used, preferably from 3 to about 150, more preferably from 6 to about 100. Suitable oxy C₄-C₆ alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents such as $\text{MO}_3\text{S}(\text{CH}_2)_n\text{OCH}_2\text{CH}_2\text{O}-$, where M is sodium and n is an integer from 4-6, as disclosed in U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink.

Polymeric soil release agents useful in the present invention also include cellulosic derivatives such as hydroxyether cellulosic polymers, copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like. Such agents are commercially available and include hydroxyethers of cellulose such as METHOCEL (Dow). Cellulosic soil release agents for use herein also include those selected from the group consisting of C₁-C₄ alkyl and C₄ hydroxyalkyl cellulose; see U.S. Patent 4,000,093, issued December 28, 1976 to Nicol, et al.

Soil release agents characterized by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C₁-C₆ vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany).

One type of preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Patent 3,959,230 to Hays, issued May 25, 1976 and U.S. Patent 3,893,929 to Basadur issued July 8, 1975.

Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units contains 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Examples of this polymer include the commercially available material ZELCON 5126 (from Dupont) and MILEASE T (from ICI). See also U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

Another preferred polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are described fully in U.S. Patent 4,968,451, issued November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Patent 4,711,730, issued December 8, 1987 to Gosselink et al, the anionic end-capped oligomeric esters of U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink, and the block polyester oligomeric compounds of U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

Preferred polymeric soil release agents also include the soil release agents of U.S. Patent 4,877,896, issued October 31, 1989 to Maldonado et al, which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters.

Still another preferred soil release agent is an oligomer with repeat units of terephthaloyl units, sulfoisoterephthaloyl units, oxyethyleneoxy and oxy-1,2-propylene units. The repeat units form the backbone of the oligomer and are preferably terminated with modified isethionate end-caps. A particularly preferred soil release agent of this type comprises about one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a ratio of from about 1.7 to about 1.8, and two end-cap units of sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said soil release agent also comprises from about 0.5% to about 20%, by weight of the oligomer, of a crystalline-reducing stabilizer, preferably selected from the group consisting of xylene sulfonate, cumene sulfonate, toluene sulfonate, and mixtures thereof.

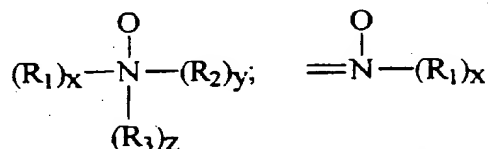
If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

Dye Transfer Inhibiting Agents - The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer

inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: $R-A_x-P$; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: $-NC(O)-$, $-C(O)O-$, $-S-$, $-O-$, $-N=$; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



wherein R_1 , R_2 , R_3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a $pK_a < 10$, preferably $pK_a < 7$, more preferred $pK_a < 6$.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".

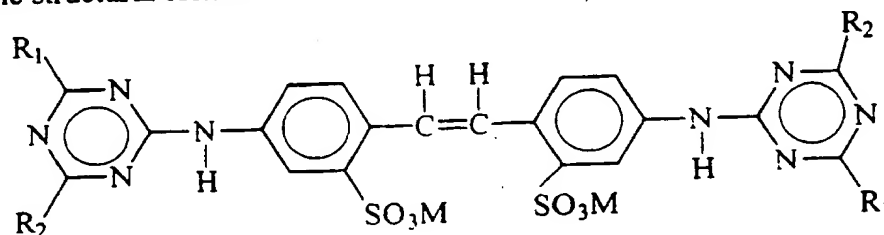
The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which has an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein R₁ is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R₂ is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino,

morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

The specific optical brightener species selected for use in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present compositions to provide

conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

Brightener - Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.05% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, available from Hilton-Davis, located in Italy; the 2-(4-styryl-phenyl)-2H-naphthol[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-bis(-venzimidazol-2-yl)ethylene; 1,3-diphenyl-phrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-naphth-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho- [1,2-d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton. Anionic brighteners are preferred herein.

Abrasives. An essential component of many hard surface cleaning compositions is the abrasive material added to facilitate the action of scouring. Abrasive scouring cleansers provide a convenient and useful means for carrying out the sanitizing of bathroom surfaces, including toilet bowls and urinals. The particulate abrasive material within such compositions serves to abrade and loosen soil adhering to hard surfaces and further serves to create more intimate contact between hard surface stain and the surfactant and/or bleaching agents also present in the cleansing compositions.

Abrasive cleaners have traditionally contained water-insoluble, relatively hard, particulate mineral material as the abrasive agent. The most common such abrasive agent is finely divided silica sand having particle size varying between about 1 and 300 microns and specific gravity of about 2.1 or higher. While such

material is generally very effective in scouring soil and stains from the surfaces being treated, abrasive material of this type tends to be difficult to rinse away from the toilet bowl or urinal surface.

It has been discovered that suitable abrasive compositions can be realized by utilizing a particular type of expanded perlite abrasive in combination with the surfactants, filler material, urease inhibitors and other optional scouring material ingredients listed herein. The abrasive materials suitable to the present invention are those contained in U.S. Pat. No. 4,051,056, Hartman, issued September 27, 1977 and included herein by reference.

The compositions herein may be in the form of granules, liquids, bars, and the like, and typically are formulated to provide an in-use pH in the range of 9 to 11. Various carriers such as sodium sulfate, water, water-ethanol, sodium carbonate, and the like, may be used routinely to formulate the finished products. Granules may be produced by spray-drying or by agglomeration, using known techniques, to provide products in the density range of 350-950 g/l. The compositions may also contain conventional perfumes, bactericides, hydrotropes and the like. If desired, conventional auxiliary builders such as citrate, zeolites (e.g., zeolites A, P, X and MAP), layered silicates (e.g., SKS-6, Hoechst) and the like can be used in the present composition at levels from 1% to 50%. Non-limiting examples of compositions according to this invention are as follows:

EXAMPLE IX

	<u>% (wt.)</u>		
	<u>A</u>	<u>B</u>	<u>C</u>
Alkyl Sulfate	9.0	7.0	7.0
Alkyl Ethoxylate Sulfate	2.0	2.0	-
Oleoyl Sarcosinate	6.0	4.0	6.0
C ₁₀ EO _{11.8} OCH ₃ ¹	4.0	6.0	4.0
2-ethylhexylPE _{7.2} OCH ₃ ²	4.0	3.0	2.0
Percarbonate	18.0	-	15.0
Tetraacetylenediamine	3.0	-	5.0
EDDS[S,S]	20.0	12.0	25.0
Lipase (Lipolase 165 KLU)	0.2	0.1	0.2
Cellulase (1000 cevu)	0.1	0.1	0.2
Endo A (5000 s-cevu)	0.2	-	-
Protease (Savinase 13 KNPU)	0.5	-	0.4
Termamyl (60T)	0.3	-	-
Alcalase (3 AU)	-	0.5	-

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Sodium Carbonate	4.0	8.0	6.0
Mg Sulfate	0.5	-	-
Maleic & Acrylic Acid Copolymer			
Sodium Salt	5.0	4.0	3.0
Carboxymethyl Cellulose, Sodium Salt	0.3	0.3	0.3
Soil Release Polymer	0.3	0.2	0.3
Polyvinyl-N-Oxide	-	0.2	-
PVP-PVPVI Copolymer	0.4	-	0.02
PEG	-	0.5	-
Brighteners, Suds Suppressors, Perfume	0.3	-	0.2
Inert Carrier and Minors		Balance	

1. Nonionic surfactant of the present invention comprising one equivalent of C10 linear alcohol derived glycidyl ether and one equivalent of polyethylene glycol monomethyl ether have an average ethoxylation of 11.8 as described in Example V.
2. Nonionic surfactant of the present invention comprising one equivalent of 2-ethylhexyl alcohol derived glycidyl ether and one equivalent of polyethylene glycol monomethyl ether have an average ethoxylation of 7.2 as described in Example III.

EXAMPLE X

A laundry bar suitable for hand-washing soiled fabrics is prepared by standard extrusion processes and comprises the following:

<u>Ingredient</u>	<u>% (wt.)</u>
C ₁₂ -C ₁₆ dimethyl hydroxyethyl ammonium chloride	10
C ₁₀ PE _{11.8} OCH ₃ ¹	15
EDDS [S,S]	15
Sodium carbonate	25
Zeolite A (0.1-10m)	5
Coconut monoethanolamide	2
Carboxymethylcellulose	0.2
Polyacrylate (m.w. 1400)	0.2
Brightener, perfume	0.2
Protease	0.3
CaSO ₄	1
MgSO ₄	1
Water	4
Filler ²	---
	--- Balance ---

1. Nonionic surfactant of the present invention comprising one equivalent of C₁₀ linear alcohol derived glycidyl ether and one equivalent of polyethylene glycol mono-methyl ether have an average ethoxylation of 11.8 as described in Example V.
2. Can be selected from convenient materials such as CaCO₃, talc, clay, silicates, and the like.

EXAMPLE XI

A liquid laundry detergent with improved grease/oil stain removal especially at 70°F (21°C) is as follows.

<u>Ingredient</u>	<u>% (wt.)</u>
C ₁₂ -C ₁₄ trimethylammonium chloride	15.0
2-butyl-C ₈ PE _{11.8} OCH ₃ ¹	10.0
EDDS	18.0
Fatty acids	3.00
Monoethanolamine	2.00
Ethoxylated tetraethylene pentamine	0.91
Protease	0.89
Boric acid	1.50
1,2-propane diol	10.00
Ethanol	7.00
Silicone suds suppressor	0.05
Water/miscellaneous	Balance

1. Nonionic surfactant of the present invention comprising one equivalent of 2-butyloctyl alcohol derived glycidyl ether and one equivalent of polyethylene glycol mono-methyl ether have an average ethoxylation of 11.8 as described in Example VI.

The foregoing composition is designed for use at 0.39 cup (92.4 mL) in a conventional U.S. top-loading automatic washing machine, or its equivalent.

EXAMPLE XII

A liquid laundry detergent composition suitable for use at the relatively high concentrations common to front-loading automatic washing machines, especially in Europe, and over a wide range of temperatures is as follows.

<u>Ingredient</u>	<u>Weight %</u>
C ₁₄ -16-N-methyl glucamide	5.0
C ₁₄ -15EO(2.25) sulfate, Na salt	5.0
Oleoyl sarcosinate, Na	10.0
C ₁₀ PE _{11.8} OCH ₃ ¹	4.0
C ₁₂ -14 alkenylsuccinic anhydride ²	4.0

C ₁₂₋₁₄ fatty acid ³	3.0
Citric acid (anhydrous)	4.6
Protease (enzyme) ⁴	0.37
Termamyl (enzyme) ⁵	0.12
Lipolase (enzyme) ⁶	0.36
CAREZYME (enzyme) ⁷	0.12
EDDS ⁸	12.0
NaOH (pH to 7.6)	5.5
1,2 propanediol	4.7
Ethanol	4.0
Sodium metaborate	4.0
CaC ₂	0.014
Ethoxylated tetraethylene pentamine ⁹	0.4
Brightener ¹⁰	0.13
Silane ¹¹	0.04
Soil release polymer ¹²	0.2
Silicone (suds control) ¹³	0.4
Silicone dispersant ¹⁴	0.2
Water and minors	Balance

1. Nonionic surfactant of the present invention comprising one equivalent of C₁₀ linear alcohol derived glycidyl ether and one equivalent of polyethylene glycol mono-methyl ether have an average ethoxylation of 11.8 as described in Example V.
2. As SYNPRAX 3 from ICI or DTSA from Monsanto.
3. Preferred fatty acid is topped palm kernel, comprising 12% oleic acid and 2% each of stearic and linoleic.
4. As Protease B as described in EPO 0342177 November 15, 1989, percentage at 40 g/l.
5. Amylase, from NOVO; percentage at 300 KNU/g.
6. Lipase, from NOVO; percentage at 100 KLU/g.
7. Cellulase from NOVO; percentage at 5000 CEVU/l.
8. Isomer mixture.
9. From BASF as LUTENSOL P6105.
10. BLANKOPHOR CPG766, Bayer.
11. Silane corrosion inhibitor, available as A1130 from Union Carbide or DYNASYLAN TRIAMINO from Hols.
12. Polyester, per U.S. Patent 4,711,730.
13. Silicone suds control agent available as Q2-3302 from Dow Corning.

14. Dispersant for silicone suds control agent available as DC-3225C from Dow Corning.

While the foregoing Examples illustrate the practice of the invention primarily with respect to fabric laundering compositions, it is to be understood that the nonionic surfactants of the present invention can also be used to advantage in hard surface cleaning compositions. If desired, such compositions may also comprise the various adjunct ingredients, preferred surfactants, and the in the case of toilet bowl and urinal cleaners various urease inhibitors. In general, however, such compositions may also comprise various ingredients whose physical properties are especially useful for specific end-uses.

A liquid toilet bowl/urinal cleaner comprising an effective amount of a urease inhibitor to inhibit the enzyme urease is prepared by standard methods and comprises the following:

EXAMPLE XIII

<u>Component</u>	<u>Formula No. (Weight %)</u>		
Isopropanol	6.0	5.4	2.0
Butoxypropanol	3.0	----	3.0
Monoethanolamine	0.50	0.40	0.50
Cocoamidopropylhydroxy sultaine	0.16	----	0.075
Sodium lauryl sulfate	0.02	----	----
C ₁₀ PE _{11.8} OCH ₃ ¹	0.60	0.90	----
2-butyl-C ₈ PE _{11.8} OCH ₃ ²	----	1.0	----
Linear alkylbenzenesulfonate	----	0.07	----
C ₉ alkylphenoethoxylate	----	0.03	----
C ₆ EO ₄ OCH ₃ ³	----	----	0.075
Sodium acetate	----	----	0.05
Ammonia	----	0.10	----
Potassium Acetohydroxamate	----	5.0	----
N-(4-aminophenyl)phosphorotriamide	2.0	----	----
N-(diaminophosphinyl)-3-pyridinecarboxamide	----	----	3.0
Perfume	0.13	----	0.11
De-ionized water	balance	balance	balance

1. Nonionic surfactant of the present invention comprising one equivalent of C₁₀ linear alcohol derived glycidyl ether and one equivalent of polyethylene glycol mono-methyl ether have an average ethoxylation of 11.8 as described in Example V.
2. Nonionic surfactant of the present invention comprising one equivalent of 2-butyloctyl alcohol derived glycidyl ether and one equivalent of polyethylene glycol mono-methyl ether have an average ethoxylation of 11.8 as described in Example VI.
3. Nonionic surfactant of the present invention comprising one equivalent of hexyl alcohol derived glycidyl ether and one equivalent of polyethylene glycol mono-methyl ether have an average ethoxylation of 4 as described in Example IV.

SURFACE WETTING TEST

Determination of the wetting ability of hard surface cleaners is important due to the short contact time these compounds have with the surfaces to be cleaned. In general, the cleaning composition is applied to the surface needing to be cleaned and then quickly wiped, scoured or scrubbed. Wetting ability on hard surfaces can be measured by comparing a solution containing a surfactant versus distilled water. One drop of each solution is placed onto a hard surface material and the wetting ability is then related to how large a "diameter of spreading" the test solution

produces compared to the distilled water control. Comparisons are also made at various surfactant concentrations to find the optimal wetting concentration. Superior wetting is indicated when the diameter of the solution drop is greater than 300% that of the pure liquid. The following tests were performed on black glossy porcelain tiles (Villeroy & Boch, Germany) at 24°C using 20% surfactant solutions in distilled water. Wetting diameter were measured 10 minutes after placement of solution drops on tile.

TABLE I
SURFACE WETTING

Surfactant	MPEG: glycidyl ether ratio	Solution appearance	Surfactant solution: water diameter ratio
De-ionized water reference	---	clear	100
C ₈₋₁₀ EO ₆	---	clear	180
C ₈ PE _{7.2} OCH ₃	1.5:1	clear	330
C ₈ PE _{7.2} OCH ₃	2:1	clear	330
C ₁₀ PE _{7.2} OCH ₃	2:1	hazy emulsion	260

SURFACE SHINE TEST

Surface filming and streaking residues are an undesirable by-product of hard surface cleaners. The following embodiments of the surfactants of the present invention were evaluated for their filming and streaking properties using the grading standards listed below. Lack of filming/ streaking on surfaces due to dilute solutions of surfactant represents another desirable property of good hard surface cleaning agents. The solutions described in the table below were diluted 1:128 with 7 gpg water to simulate actual usage conditions. The dilute solutions were applied in equal concentration to black, clean polyurethane tiles (Mannington checkmate-black 215) and allowed to dry for 2 hours. Three expert panelists were then asked to grade the filming/ streaking residues left on by the dried surfactant solutions. Comparisons were made versus a high performance benchmark control product (i.e., a product which displays good shine end result properties). Surprisingly, the prototypes using surfactants of this invention displayed even better filming/ streaking profiles.

TABLE II
SURFACE SHINE

weight %			
Ingredients	Reference	A	B
C ₈ -C ₁₀ EO ₆	20	--	--
2-ethylhexylPE _{7.2} OCH ₃	--	20	--
C ₈ PE _{11.8} OCH ₃	--	--	20
C ₁₂ -C ₁₃ EO ₃	4	4	4
sodium carbonate	1	1	1
C ₈ -C ₁₈ fatty acid	0.6	0.6	0.6
pH adjusted to 10	--	--	--
dilute 1:128 with H ₂ O	--	--	--
Filming/Streaking Grade	Control	+1.3	+2.1

GRADING SCALE

0: I see no difference in the level of residue left by the experimental and control products.

+1: I think the experimental prototype leaves a less noticeable residue than the control formula.

-1: I think the control formula leaves a less noticeable residue than the experimental prototype.

+2: I know the experimental prototype leaves a slightly less noticeable residue than the control formula.

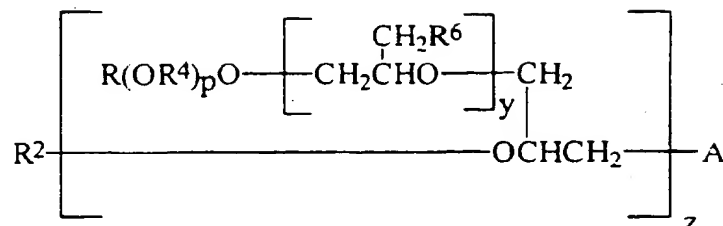
-2: I know the control formula leaves a slightly less noticeable residue than the experimental prototype.

+3: I know the experimental prototype leaves a much less noticeable residue than the control formula.

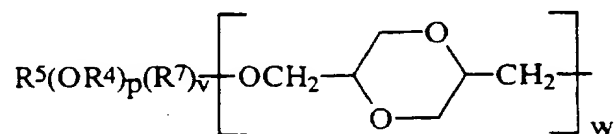
-3: I know the control formula leaves a much less noticeable residue than the experimental prototype.

What is claimed is:

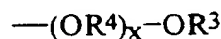
1. A nonionic surfactant of the formula:



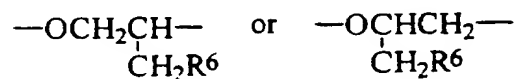
wherein R is C₁-C₂₂ linear alkyl, C₃-C₂₂ branched alkyl, C₃-C₂₂ linear alkenyl, C₃-C₂₂ branched alkenyl, C₅-C₂₂ cyclic alkyl, C₅-C₂₂ cyclic alkenyl, aryl or C₁-C₂₂ alkyl substituted aromatic, preferably C₆-C₁₈ linear alkyl, C₆-C₁₈ linear alkenyl or C₆-C₂₂ branched alkyl; R² is hydrogen, C₁-C₄ alkyl, preferably hydrogen or when z = 0 the formula:



wherein R⁴ is C₂-C₄ alkylene, preferably ethylene or propylene; R⁵ is hydrogen or R; A has the formula:



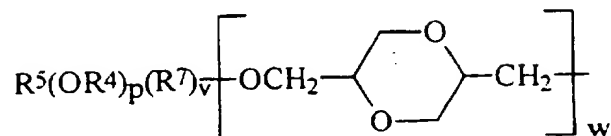
wherein R³ is hydrogen or R, preferably C₁-C₁₈ alkyl, C₆-C₁₈ alkenyl, or C₆-C₂₂ branched alkyl; R⁷ has the formula:



wherein R⁶ is A, halogen, or hydroxyl; p is from 0 to 100; v is 0 or 1; w is 0 or 1; x is from 0 to 100, preferably from 3 to 25; y is from 0 to 2; z is from 0 to 3; w + z is at least 1.

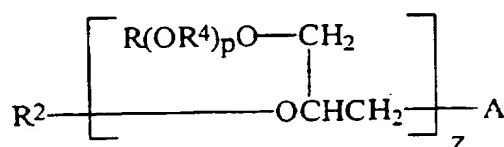
-63-

2. A surfactant according to Claim 1 wherein R^2 is hydrogen or has the formula



wherein R^5 is hydrogen or C_1 - C_4 alkyl; v is equal to 0; p is from 0 to 100; w is equal to 0; and y is equal to 0.

3. A process for preparing a nonionic surfactant of the formula:

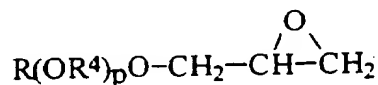


wherein A has the formula:

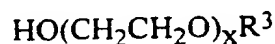


wherein x is from 0 to 100; p is from 0 to 100; z is equal to 1; R^2 is hydrogen or C_1 - C_4 alkyl, C_2 - C_4 hydroxyalkyl, poly(C_2 - C_4 oxyalkylene), preferably hydrogen; R^3 is C_1 - C_4 alkyl or C_3 - C_4 alkenyl, preferably methyl; R^4 is C_2 - C_4 alkylene; comprising the steps of:

- a) reacting a glycidyl ether of the formula



wherein R is C_1 - C_{22} linear alkyl, C_3 - C_{22} branched alkyl, C_3 - C_{22} linear alkenyl, C_3 - C_{22} branched alkenyl, C_5 - C_{22} cyclic alkyl, aryl or C_1 - C_{22} alkyl substituted aryl, preferably C_6 - C_{18} linear alkyl or branched alkyl; with an alkyl capped polyethylene glycol of the formula:

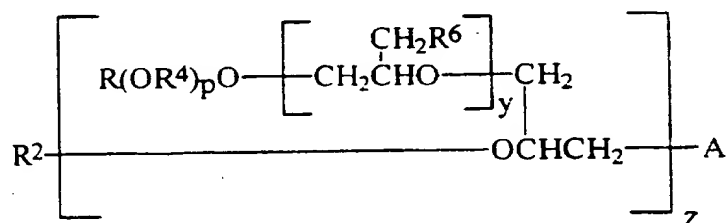


wherein R^3 , p and x are as defined above; in the presence of a base to form a crude alkaline nonionic surfactant reaction product;

- b) neutralizing the crude alkaline nonionic surfactant reaction product formed in step (a) to form a crude nonionic surfactant reaction product;

- c) optionally further reacting the reaction product of either step (a) or (b) with:
- i) an alkylating agent whereby R^2 is converted to a C_1 - C_4 alkyl moiety; said alkyl moiety selected from the group consisting of methyl, ethyl, propyl, butyl, and mixtures thereof; or
 - ii) a C_2 - C_4 alkylene oxide whereby R^2 is converted to an C_2 - C_4 hydroxyalkyl moiety or polyoxyalkylene moiety;
- d) optionally purifying the reaction product formed in step (b); or
- e) optionally purifying the reaction product formed in step (c).

4. A process for preparing a nonionic surfactant of the formula:

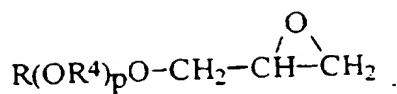


wherein R^2 is hydrogen, C_1 - C_4 alkyl, C_2 - C_4 hydroxyalkyl, C_2 - C_4 hydrogen polyoxyalkylene, and mixtures thereof; R^6 is halogen, preferably chlorine; A has the formula:

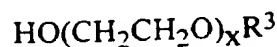


wherein R^3 is C_1 - C_4 alkyl or C_3 - C_4 alkenyl; x is from 0 to 100; p is from 0 to 100; y is 0, 1 or 2; z is from 0 to 3; w + z is at least 1; comprising the steps of:

- a) reacting an alcohol of the formula $\text{R(OR}^4\text{)}_p\text{OH}$ wherein R is C_1 - C_{22} linear alkyl, C_3 - C_{22} branched alkyl, C_5 - C_{22} cyclic alkyl, C_5 - C_{22} alkenyl, aromatic, or C_1 - C_{22} alkyl substituted aromatic; with an epihalohydrin in the presence of an acid catalyst, preferably boron trifluoride, boron trifluoride etherate, titanium tetrachloride, stannic chloride, preferably in a mole ratio of epihalohydrin to $\text{R(OR}^4\text{)}_p\text{OH}$ greater than or equal to 1:1, followed by treatment with a base, to form a glycidyl ether of the formula

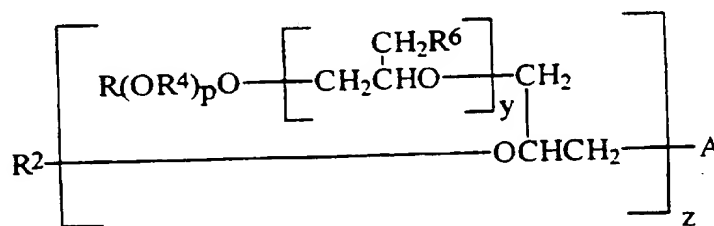


- b) reacting the glycidyl ether formed in step (a) with a C₁-C₄ alkyl capped polyethylene glycol ether of the formula:



- wherein R³ and x is the same as defined above, in the presence of an acidic catalyst to form a crude nonionic surfactant reaction product;
- c) neutralizing acidic reaction product formed in step (b) to form a crude nonionic surfactant product;
- d) optionally further reacting the reaction product of step (c) wherein R² is hydrogen with
- i) an alkylating agent whereby R² is converted to a C₁-C₄ alkyl moiety; said alkyl moiety selected from the group consisting of methyl, ethyl, propyl, butyl, and mixtures thereof; or
 - ii) a C₂-C₄ alkylene oxide whereby R² is converted to an C₂-C₄ hydroxyalkyl moiety or polyoxyalkylene moiety;
- e) optionally purifying the reaction product formed in step (c); or
- f) optionally purifying the reaction product formed in step (d).

5. A process for preparing nonionic surfactants of the formula:

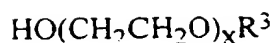


wherein R is C₁-C₂₂ linear alkyl, C₃-C₂₂ branched alkyl, C₃-C₂₂ linear alkenyl, C₃-C₂₂ branched alkenyl, C₅-C₂₂ cyclic alkyl, C₅-C₂₂ cyclic alkenyl, aryl or alkyl substituted aromatic; R² is hydrogen, or C₁-C₄ alkyl, preferably hydrogen; A has the formula:



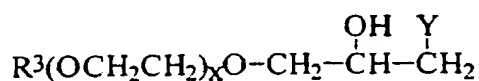
wherein R³ is C₁-C₄ alkyl; x is 2 to 100; y is 0, 1 or 2; z is 1, 2 or 3; comprising the steps of:

- a) reacting an alkyl capped polyethylene glycol of the formula:



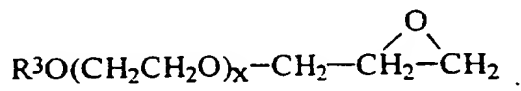
wherein R^3 is C_1 - C_4 alkyl; x is from 2 to 100; and an epihalohydrin in the presence of acid catalyst to form an acidic crude polyethylene glycol halohydrin reaction product;

- b) neutralizing the acidic reaction product of step (a) to form a crude polyethylene glycol halohydrin reaction product of the formula



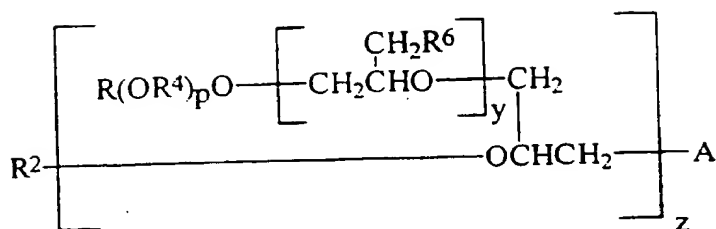
wherein Y is chlorine, bromine, or iodine;

- c) optionally purifying the crude polyethylene glycol halohydrin reaction product formed in step (b);
- d) reacting the polyethylene glycol halohydrin reaction product of step (b) or step (c) with at least one equivalent of base to form a glycidyl ether of the formula

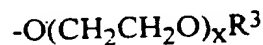


- e) reacting the glycidyl ether formed in step (d) with an alcohol $\text{R}(\text{OR}^4)_p\text{OH}$ wherein R is C_1 - C_{22} linear alkyl, C_3 - C_{22} branched C_3 - C_{22} linear alkenyl, C_3 - C_{22} branched alkenyl, C_5 - C_{22} cyclic alkyl, aryl or C_1 - C_{22} alkyl substituted aryl; in the presence of sufficient base to form an alkaline crude nonionic surfactant reaction product;
- f) neutralizing the alkaline reaction product formed in step (e) to form a crude nonionic surfactant reaction product;
- g) optionally further reacting the reaction product of step (f) wherein R^2 is hydrogen with
- i) an alkylating agent whereby R^2 is converted to a C_1 - C_4 alkyl moiety; said alkyl moiety selected from the group consisting of methyl, ethyl, propyl, butyl, and mixtures thereof; or
 - ii) a C_2 - C_4 alkylene oxide whereby R^2 is converted to an C_2 - C_4 hydroxyalkyl moiety or polyoxyalkylene moiety;
- h) optionally purifying the reaction product formed in step (f); or
- i) optionally purifying the reaction product formed in step (g).

6. A process for preparing nonionic surfactants of the formula:

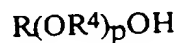


wherein R is C₁-C₂₂ linear alkyl, C₃-C₂₂ branched alkyl, C₃-C₂₂ linear alkenyl, C₃-C₂₂ branched alkenyl, C₅-C₂₂ cyclic alkyl, C₅-C₂₂ cyclic alkenyl, aryl or alkyl substituted aromatic; R² is hydrogen, C₁-C₄ alkyl, C₁-C₄ polyoxyalkylene, or mixtures thereof; A has the formula:

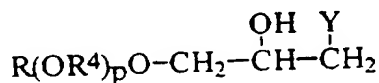


wherein R³ is C₁-C₄ alkyl; R⁴ is C₂-C₄ alkylene; x is 2 to 100; y is 0, 1 or 2; z is 1, 2 or 3; comprising the steps of:

a) reacting an alcohol of the formula:

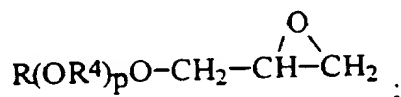


the wherein R, R⁴ and x are as defined above; and an epihalohydrin in presence of acid catalyst, preferably boron trifluoride, boron trifluoride etherate, titanium tetrachloride or stannic chloride, to form an acidic crude halohydrin reaction product of the formula

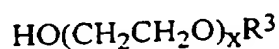


wherein Y is chlorine, bromine, or iodine;

- b) optionally purifying the crude halohydrin reaction product formed in step (a);
- c) reacting the halohydrin reaction product of step (a) or step (b) with at least one equivalent of base to form a glycidyl ether of the formula



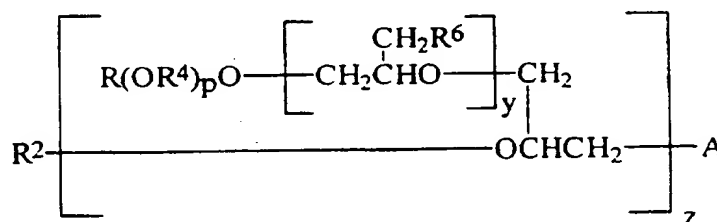
- d) reacting the glycidyl ether formed in step (c) with a capped polyethylene glycol of the formula



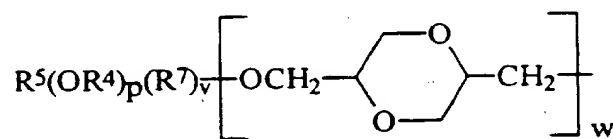
-68-

- wherein R^3 is C_1 - C_4 alkylene; x is from 2 to 100; in the presence of sufficient base to form an alkaline crude nonionic surfactant reaction product;
- e) optionally neutralizing the alkaline reaction product formed in step (d) to form a crude nonionic surfactant reaction product;
 - f) optionally further reacting the reaction product of step (d) or (e) with
 - i) an alkylating agent whereby R^2 is converted to a C_1 - C_4 alkyl moiety; said alkyl moiety selected from the group consisting of methyl, ethyl, propyl, butyl, and mixtures thereof; or
 - ii) a C_2 - C_4 alkylene oxide whereby R^2 is converted to an C_2 - C_4 hydroxyalkyl moiety or polyoxyalkylene moiety;
 - g) optionally purifying the reaction product formed in step (e); or
 - h) optionally purifying the reaction product formed in step (f).

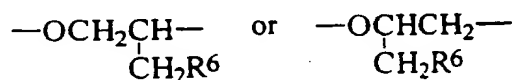
7. A process for preparing a nonionic surfactant of the formula:



wherein R^2 has the formula



R^7 has the formula:



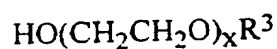
wherein R^6 is R or halogen; A has the formula:



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wherein R^3 is C_1 - C_4 alkyl or C_3 - C_4 alkenyl; x is from 0 to 100; p is from 0 to 100; v is 0 or 1; w is 0 or 1; x is from 2 to 100; y is 0, 1 or 2; z is from 0 to 3; comprising the steps of:

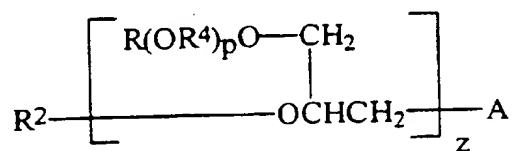
- a) reacting an alcohol of the formula ROH wherein R is C_1 - C_{22} linear alkyl, C_4 - C_{22} branched alkyl, C_5 - C_{22} cyclic alkyl, C_5 - C_{22} alkenyl, aromatic, or C_1 - C_{22} alkyl substituted aromatic; with 1 to 5 equivalents of an epihalohydrin in the presence of an acid catalyst followed by treatment with sufficient base to form a crude glycidyl ether mixture;
- b) reacting the crude glycidyl ether mixture formed in step (a) with 1 to 3 equivalents of a C_1 - C_4 alkyl capped polyethylene glycol ether of the formula:



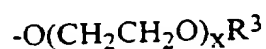
wherein R^3 and x are the same as defined above, with a base catalyst to form a crude nonionic surfactant reaction mixture;

- c) neutralizing alkaline reaction mixture formed in step (b) to form a crude nonionic surfactant product;
- d) isolating the reaction product formed in step (c); or
- e) optionally further reacting the reaction product of step (c) or step (d) wherein R^2 is hydrogen with
 - i) an alkylating agent whereby R^2 is converted to a C_1 - C_4 alkyl moiety; said alkyl moiety selected from the group consisting of methyl, ethyl, propyl, butyl, and mixtures thereof; or
 - ii) a C_2 - C_4 alkylene oxide whereby R^2 is converted to an C_2 - C_4 hydroxyalkyl moiety or polyoxyalkylene moiety; and
- f) isolating the reaction product formed in step (e).

8. A process for preparing a nonionic surfactant of the formula:



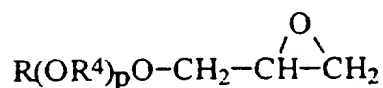
wherein A has the formula:



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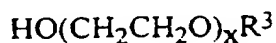
wherein x is from 0 to 100; p is from 0 to 100; z is equal to 1; R² is hydrogen or C₁-C₄ alkyl, C₂-C₄ hydroxyalkyl, poly(C₂-C₄ oxyalkylene), preferably hydrogen; R³ is C₁-C₄ alkyl or C₃-C₄ alkenyl, preferably methyl; R⁴ is C₂-C₄ alkylene; comprising the steps of:

- a) reacting a glycidyl ether of the formula



linear
C₂₂
alkyl;

wherein R is C₁-C₂₂ linear alkyl, C₃-C₂₂ branched alkyl, C₃-C₂₂ alkenyl, C₃-C₂₂ branched alkenyl, C₅-C₂₂ cyclic alkyl, aryl or C₁-alkyl substituted aryl, preferably C₆-C₁₈ linear alkyl or branched with an alkyl capped polyethylene glycol of the formula:



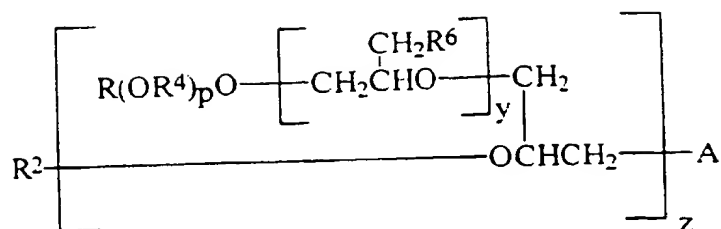
wherein R³, p and x are as defined above; in the presence of a base to form a crude alkaline nonionic surfactant reaction product;

- b) neutralizing the crude alkaline nonionic surfactant reaction product formed in step (a) to form a crude nonionic surfactant reaction product;
- c) optionally further reacting the reaction product of either step (a) or (b) with:
- i) an alkylating agent whereby R² is converted to a C₁-C₄ alkyl moiety; said alkyl moiety selected from the group consisting of methyl, ethyl, propyl, butyl, and mixtures thereof; or
 - ii) a C₂-C₄ alkylene oxide whereby R² is converted to an C₂-C₄ hydroxyalkyl moiety or polyoxyalkylene moiety;
- d) optionally purifying the reaction product formed in step (b); or
- e) optionally purifying the reaction product formed in step (c).

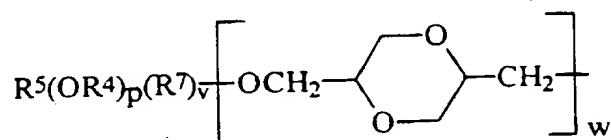
9. A cleaning composition comprising:

- a) at least 0.01% of a nonionic surfactant having the formula

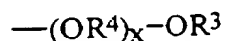
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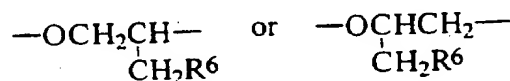
wherein R is C₁-C₂₂ linear alkyl, C₃-C₂₂ branched alkyl, C₅-C₂₂ cyclic alkyl, C₆-C₁₄ aromatic, C₁-C₂₂ alkyl substituted aromatic, and mixtures thereof; R² is hydrogen, C₁-C₄ alkyl or the formula:



wherein R⁴ is C₂-C₄ alkylene; R⁵ is hydrogen or R; A has the formula:



wherein R³ is hydrogen, C₁-C₂₂ alkyl or alkenyl; R⁷ has the formula:



wherein R⁶ is halogen, or hydroxyl; p is from 0 to 100; v is 0 or 1; w is 0 or 1; x is from 0 to 100; y is from 0 to 2; z is from 0 to 3; w + z is at least 1;

- b) a deterative surfactant, preferably from 0.1% to 50%, more preferably from 1% to 10% by weight; and
- b) carriers and adjunct ingredients

10. A cleaning composition according to Claim 9 wherein the adjunct ingredients are selected from the group consisting of anionic surfactants, cationic surfactants, nonionic surfactants, zwitterionic surfactants, ampholytic surfactants, enzymes, enzymes stabilizers, bleaches, bleach activators, builders, soil release agents, chelants, anti-redeposition agents, dispersants, brighteners, suds suppressors, fabric softeners, dye transfer inhibitors, abrasives, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/JS 96/20776

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08G65/26 C11D1/72 C08L71/02 C08G65/32

According to International Patent Classification (IPC) or to both national classification and IPC:

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G C11D C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 294 365 A (WELCH MICHAEL C ET AL) 15 March 1994 see claim 1 see example 1 see column 2, line 13 see column 4, line 25 - line 40 see column 2, line 60 - column 3, line 3 ---	1-4,6-10
X	DE 31 44 371 A (BASF AG) 9 June 1982 see claims 1-3; example 1 ---	1,5
X	US 4 354 956 A (CAMP RONALD L) 19 October 1982 see claim 1 ---	1
A	EP 0 322 110 A (MILLIKEN RES CORP) 28 June 1989 see claim 1 ---	1,2,7,9, 10
-/-		

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

- * "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- * "&" document member of the same patent family

Date of the actual completion of the international search

25 April 1997

Date of mailing of the international search report

26.05.97

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O'Sullivan, T

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 96/20776

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 278 120 A (WARNSTAR LIMITED) 23 November 1994 see claims 1,2 see page 21, line 28 -----	1,2,7,9, 10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 96/20776

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5294365 A	15-03-94	NONE	
DE 3144371 A	09-06-82	CA 1173861 A US 4375565 A	04-09-84 01-03-83
US 4354956 A	19-10-82	US 4288639 A CA 1156676 A	08-09-81 08-11-83
EP 0322110 A	28-06-89	US 4977281 A AT 121429 T CA 1308850 A DE 3853623 D DE 3853623 T JP 2000283 A US 4985546 A	11-12-90 15-05-95 13-10-92 24-05-95 07-09-95 05-01-90 15-01-91
GB 2278120 A	23-11-94	NONE	